10 ; 5 ° 1 8 4 3

R'e'd PCT/PTO *18* JAN 2005

Description

Dendritic Polymer and Electronic Device Element Employing the Polymer

Technical Field

The present invention relates to a novel dendritic polymer——dendrimer or hyperbranched polymer——having carrier conductivity, and to an electronic device employing the dendritic polymer. The dendritic polymer of the present invention attains high carrier conduction at remarkably high efficiency, and thus finds utility particularly in devices requiring carrier conductivity; e.g., switching elements such as organic transistors (organic FETs, organic TFTs, etc.), solar cells, and organic EL devices.

Background Art

Electrically conductive organic polymers have become of scientific and technical interest since the late 1970s. The polymers, which are based on a comparatively new technique, exhibit electronic and magnetic characteristics of metal as well as physical and mechanical characteristics of conventional organic polymers. Known conductive organic polymers include poly(p-phenylene)s, poly(p-phenylenevinylene)s, polyanilines, polythiophenes, polypyrroles, polyazines, polyfurans, polycenophenes, poly(p-phenylene sulfide)s, mixtures thereof, blends thereof with

another polymer, and copolymers of monomers of the above-
described polymers. These conductive organic polymers are
conjugated-system polymers which exhibit electrical
conductivity through doping caused by reaction such as
5   oxidation, reduction, or protonization.

In recent years, efforts have been made to fabricate,
from these conductive organic polymers, light-emitting
elements of organic electroluminescent devices (organic EL,
OLED) and active elements of field-effect transistors
10 (organic FET, organic TFT). In one current practice, an
expensive plasma CVD apparatus is used for forming an
insulating layer or a semiconductor layer of an amorphous
silicon TFT or polysilicon TFT, and an expensive sputtering
apparatus is used for forming an electrode. In addition,
15 film formation by CVD must be carried out at a temperature as
high as 230 to 350°C, and maintenance operations such as
cleaning must be carried out frequently, thereby reducing
throughput. In contrast, apparatuses such as a coating
apparatus and an ink-jet apparatus for fabricating organic
20 FETs or similar devices are less expensive than the CVD
apparatus and sputtering apparatus. In addition, film
formation can be performed at lower temperature, and
maintenance of the apparatuses is less cumbersome. Therefore,
when display devices such as a liquid crystal display and an
25 organic EL are fabricated from an organic FET, a remarkable
cost reduction can be expected.

Typical organic EL devices include a transparent

substrate made of material such as glass, a transparent
electrode, a hole-injecting layer, a hole-transporting layer,
a light-emitting layer, an electron-transporting layer, and a
metal electrode. Three separate layers; namely, the hole-
5   transporting layer, the light-emitting layer, and the
electron-transporting layer, may be formed into a single
hole-transporting and light-emitting layer, or into a single
electron-transporting and light-emitting layer. The specific
features are disclosed by Japanese Patent Application Laid-
10   Open (kokai) Nos. 7-126616, 8-18125, 10-92576, etc. However,
problems such as service life still remain unsolved for
organic EL devices, and studies for improvement are under way.

Typical organic TFTs include a transparent substrate
made of material such as glass, a gate substrate, a gate
15   insulating film, a source electrode, a drain electrode, and
an organic semiconductor film. By modifying gate voltage,
electric charge at the interface between the gate insulating
layer and the organic semiconductor film is rendered
excessive or deficient, whereby the drain current flowing
20   between the source and drain electrodes via the organic
semiconductor film is varied, to thereby perform switching.

Japanese Patent Application Laid-Open (kokai) No. 63-
076378 discloses that an organic TFT is fabricated from
polythiophene or a polythiophene derivative serving as the
25   aforementioned organic semiconductor film. Fabrication of an
organic TFT from pentacene is disclosed in Yen-Yi Lin, David
J. Gundlach, Shelby F. Nelson, and Tomas N. Jackson, IEEE

Transaction on Electron Device, Vol. 44, No. 8, p. 1,325 (1997).

However, use of pentacene raises problems. For example, film formation must be performed through a vapor deposition

5   process, and crystallinity must be elevated for enhancement of device characteristics. Another possible approach is use of a soluble pentacene derivative for enhancing processability. However, in this case, characteristics remain unsatisfactory.

10   Application and development of an organic semiconductor formed of polythiophene, a polythiophene derivative, or a thiophene oligomer are under way, since the organic semiconductor has excellent formability; e.g., is readily formed into thin film through electrolytic polymerization,

15   solution coating, or a similar method. However, in this case, characteristics remain unsatisfactory.

Meanwhile, in recent years, hyperbranched polymer materials in a broad sense such as dendrimers and hyperbranched polymers have become of interest.

20   Characteristic features of dendrimers and hyperbranched polymers include amorphousness, solubility in organic solvent, and presence of a large number of branch ends to which a functional group can be introduced. L. L. Miller et al. describe in J. Am. Chem. Soc. 1997, 119, 1,005 that a

25   polyamide dendrimer having, at branch ends, 1,4,5,8-naphthalenetetracarboxy-diimido residues to which a quaternary pyridinium salt is bonded has isotropic electron

conductivity (also referred to as "transportability"), and that the conductivity is provided by interaction of π electrons generated by spatial overlapping of the branch end moieties. Japanese Patent Application Laid-Open (*kokai*) No.

5   2000-336171 discloses a dendrimer containing a dendron having hole-conducting moieties at branch ends and no π-electron-conjugated system including a carbonyl group and a benzene ring, as well as a photoelectric conversion device employing the dendrimer.

10   However, in function elements employing semiconductive or conductive polymers such as conjugated polymers, high charge conductivity of the aforementioned organic semiconductor appears along a molecular chain orientation, and varies depending on the molecular structure. In addition,

15   semiconductive or conductive polymers such as conjugated polymers are generally rigid and cannot be dissolved or melted. Most of them cannot be dissolved in solvent. To this end, there are used derivatives of such polymers into which side chains are introduced, and oligomers thereof (see

20   Japanese Patent Application Laid-Open (*kokai*) Nos. 4-133351, 63-076378, 5-110069, etc.). However, problems also arise. For example, when side chains are introduced, glass transition temperature appears, and thermochromism attributed to micro-Brownian motion is induced, resulting in

25   temperature-dependent variation in characteristics. Use of oligomers may deteriorate reliability. Even when the side-chain-introduced polymer is used, satisfactory mobility

cannot be attained.   Thus, polymerization degree must be

increased, or orientation degree of the conductive organic

compound must be enhanced by use of orientation film as

described in, for example, Japanese Patent Application Laid-

5   Open (*kokai*) No. 7-206599.

Furthermore, since conjugated polymers tend to be

affected by oxygen and water, thereby readily causing

deterioration, conventional organic FET elements employing

the conjugated polymers have poor stability and electric

10   characteristics and a short service life, which is

problematic.

Meanwhile, a hyperbranched polymer having a thienylene-

phenylene structure as a structural repeating unit is

disclosed in literature (Japanese Patent No. 3074277B).

15   However, the disclosed compounds are used as conducting

materials after being doped with an electron-accepting

reagent to thereby form conductivity-imparted polymer.   Since

the production method disclosed in this document employs

polymerization based on the Grignard reaction, such a highly

20   regulated repeating structure as a dendrimer has cannot be

obtained.   Thus, the compound synthesized through this method

has a wide molecular weight distribution profile, as is the

case with customary polymers.   In addition, when functional

groups are attempted to be introduced to a core serving as a

25   center moiety or end groups serving as a molecular surface,

these functional groups are introduced randomly, raising a

problem that a desired function is difficult to attain.

Disclosure of the Invention

The present invention has been made in order to solve
the aforementioned problems arising in conventional

5   techniques. Thus, an object of the present invention is to
provide a novel dendritic polymer serving as an organic
semiconductor material which is isotropic and which exhibits
remarkably high carrier conductivity. Another object of the
invention is to provide an electronic device employing the

10 dendritic polymer.

The present inventors have carried out extensive
studies in order to solve the aforementioned problems, and
have found that a dendritic polymer produced from a repeating
unit containing at least one thienylene moiety possesses

15 semiconducting characteristics and can serve, without
requiring doping, as an organic semiconductor material which
is isotropic and which exhibits remarkably high carrier
conductivity. The present invention has been accomplished on
the basis of this finding.

20   Accordingly, a first mode of the present invention to
solve the aforementioned problems is drawn to a dendritic
polymer having a branching structure including repeating
units each having a branch portion, each of said repeating
units having a structure represented by formula (1), and

25 containing a linear portion X formed of an optionally
substituted divalent organic group and a branch portion Y
formed of an optionally substituted trivalent organic group:

—X—Y<   (1)
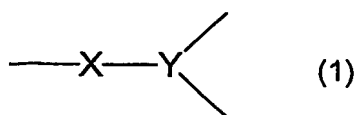
characterized in that the linear portion X contains at least
one thienylene moiety and is at least partially conjugated
with the branch portion Y, and in that the polymer reversibly
assumes an insulative state and a metallic state, depending
5   on the presence of an external factor.

A second mode of the present invention is directed to a
dendritic polymer mentioned in relation to the first mode,
wherein the external factor is electricity.

A third mode of the present invention is directed to a
10 dendritic polymer mentioned in relation to the first mode,
wherein the external factor is photoexcitation.

A fourth mode of the present invention is directed to a
dendritic polymer mentioned in relation to any one of the
first to third modes, containing substantially no doping
15 reagent.

A fifth mode of the present invention is directed to a
dendritic polymer mentioned in relation to any one of the
first to fourth modes, wherein the portion X included in the
repeating unit and serving as a starting point of the
20 branching structure is further bonded to a center moiety
serving as a core.

A sixth mode of the present invention is directed to a
dendritic polymer mentioned in relation to the fifth mode,
wherein the core is a group having a valence of at least two

to which at least two of the repeating unit can be directly bonded.

A seventh mode of the present invention is directed to a dendritic polymer mentioned in relation to any one of the first to sixth modes, wherein the portion Y included in the repeating unit and serving as an end of the branching structure is bonded to end moieties which are different from the repeating unit.

A eighth mode of the present invention is directed to a dendritic polymer mentioned in relation to any one of the first to seventh modes, wherein the branch portion Y includes, as a branching center, a chemical entity selected from among chain hydrocarbons (aliphatic hydrocarbons), cyclic hydrocarbons (including alicyclic compounds and aromatic compounds), and heterocyclic compounds (including aromatic heterocyclic compounds and non-aromatic heterocyclic compounds).

A ninth mode of the present invention is directed to a dendritic polymer mentioned in relation to the eighth mode, wherein the branch portion Y is selected from among the moieties represented by formula (2):
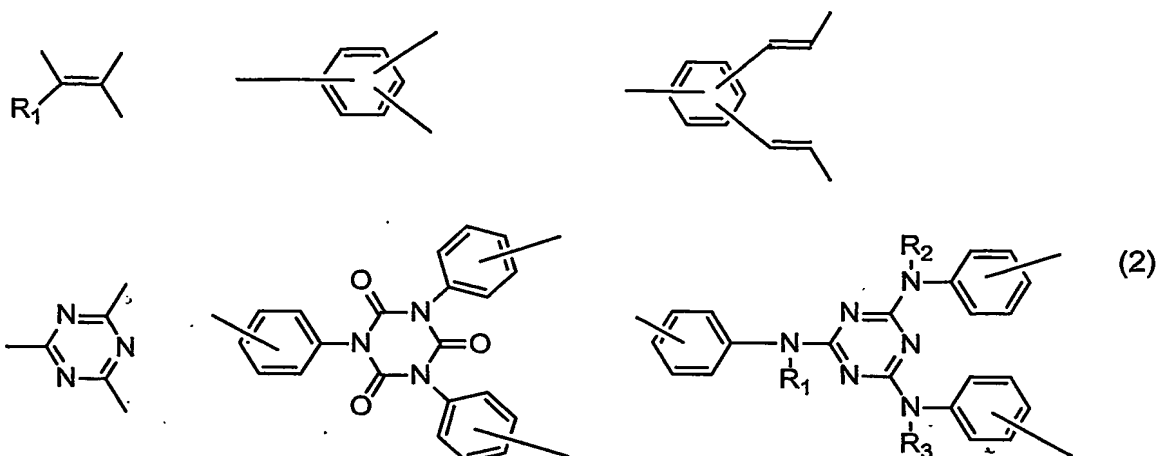
wherein each of R_1, R_2, and R_3 represents a hydrogen atom or an alkyl group.

A tenth mode of the present invention is directed to a dendritic polymer mentioned in relation to any one of the first to ninth modes, wherein the linear portion X is represented by formula (3), and is at least partially conjugated with the branch portion Y:
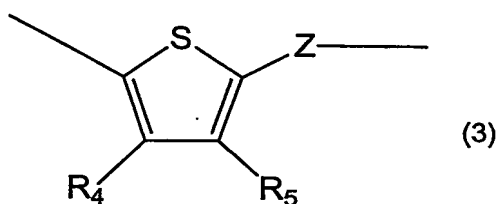
wherein Z represents a single bond or an optionally substituted divalent organic group which is at least partially conjugated with thienylene; and each of R_4 and R_5 is selected from hydrogen, an alkyl group, and an alkoxy group.
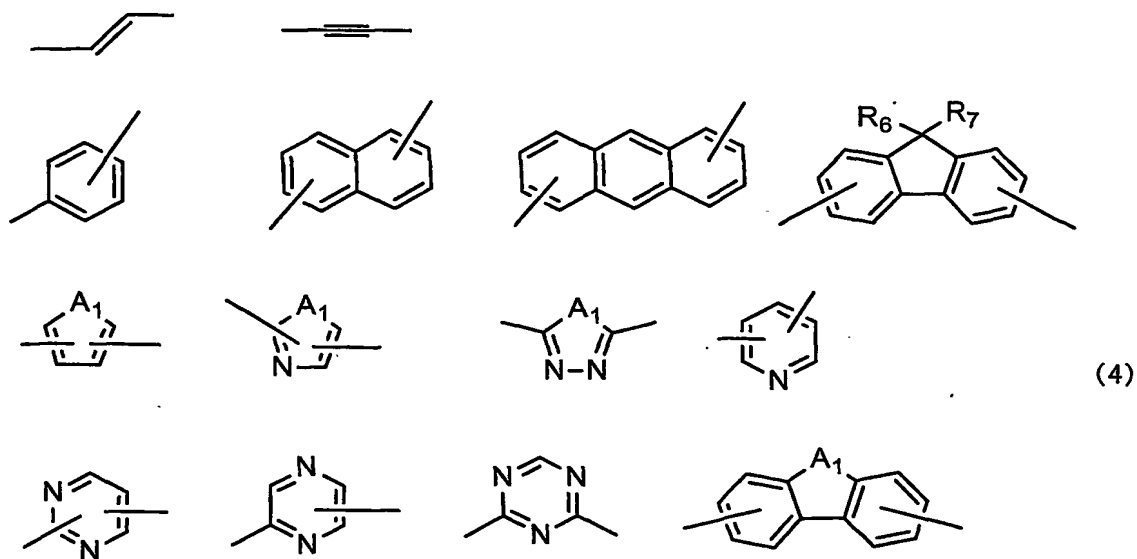
An eleventh mode of the present invention is directed to a dendritic polymer mentioned in relation to the tenth mode, wherein the substituent Z is a substituent formed from

a moiety selected from the group consisting of substituted or

unsubstituted chain hydrocarbon (aliphatic hydrocarbon)

moieties, substituted or unsubstituted cyclic hydrocarbon

(including alicyclic compound and aromatic compound) moieties,

5   and substituted or unsubstituted heterocyclic compound

(including aromatic heterocyclic compound and non-aromatic

heterocyclic compound) moieties; a substituent formed from a

plurality of same moieties continuously linked together

selected from said group; or a substituent formed from a

10   plurality of different moieties continuously linked together

selected from said group.

A twelfth mode of the present invention is directed to

a dendritic polymer mentioned in relation to the eleventh

mode, wherein the substituent Z is a substituent formed from

15   a moiety selected from the group consisting of substituted or

unsubstituted unsaturated aliphatic hydrocarbon moieties and

substituted or unsubstituted cyclic or heterocyclic aromatic

compound moieties; a substituent formed from a plurality of

same moieties continuously linked together selected from said

20   group; or a substituent formed from a plurality of different

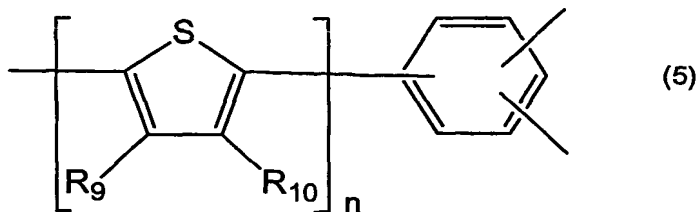moieties continuously linked together selected from said

group.

A thirteenth mode of the present invention is directed

to a dendritic polymer mentioned in relation to the twelfth

25   mode, wherein the substituent Z is a substituent formed from

a moiety selected from the group represented by formula (4);

a substituent formed from a plurality of same moieties

continuously linked together selected from said group; or a

substituent formed from a plurality of different moieties

continuously linked together selected from said group:

(4)

wherein A_1 represents O, S, or $N-R_8$, and each of R_6, R_7,

5   and R_8 represents a hydrogen atom or an alkyl group.

An fourteenth mode of the present invention is directed

to a dendritic polymer mentioned in relation to any one of

the first to ninth modes, wherein the repeating unit is

represented by formula (5):

(5)

10   wherein each of R_9 and R_{10} is selected from hydrogen, an alkyl

group, and an alkoxy group, and n represents an integer of 1

to 10.

A fifteenth mode of the present invention is directed

to a dendritic polymer mentioned in relation to any one of the first to fourteenth modes, which is a dendrimer.

A sixteenth mode of the present invention is directed to an electronic device element characterized by employing a dendritic polymer as recited in relation to any one of the first to fifteenth modes.

A seventeenth mode of the present invention is directed to an electronic device element mentioned in relation to the sixteenth mode, which is a charge-transporting device element.

A eighteenth mode of the present invention is directed to an electronic device element mentioned in relation to the sixteenth mode, which is a switching transistor element.

A nineteenth mode of the present invention is directed to an electronic device element mentioned in relation to the sixteenth mode, which is a light-emitting device element.

A twentieth mode of the present invention is directed to an electronic device element mentioned in relation to the sixteenth mode, which is a photoelectric conversion device element.

Brief Description of the Drawings

FIG. 1 schematically shows a cross-section of an organic thin film switching transistor according to Example 1 of the present invention.

FIG. 2 is a schematic view showing a light-emitting element according to Example 2 of the present invention.

FIG. 3 is a schematic view showing an organic solar

cell element according to Example 3 of the present invention.

FIG. 4 is a schematic view showing an organic solar cell element according to Comparative Example 3.

FIG. 5 is a schematic view showing an organic

5 rectifying element according to Example 4 of the present invention.

FIG. 6 is a graph showing an investigated current-voltage characteristic of the organic rectifying element according to Example 4.

10 FIG. 7 is a graph showing an investigated current-voltage characteristic of the organic rectifying element according to Comparative Example 4.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

15 The present invention will next be described in detail.

In the present invention, the term "dendritic polymer" conceptually refers to a polymer species which includes generally defined dendrimers and hyperbranched polymers. Thus, the dendritic polymer encompasses any compounds having

20 a structure in which the aforementioned structural repeating unit represented by formula (1) (i.e., dendritic structural unit) is repeated once or more (i.e., the dendritic polymer contains two or more repeating units). Notably, a structure including the aforementioned structural repeating unit

25 represented by formula (1); i.e., a structure including the repeating units repeated with the divergence-shaped, is referred to as a "branching structure."

Dendrimer and hyperbranched polymers are generally
represented by the following structural formulas. As shown
in the formulas, the dendrimer has a regularly repeated
branching structure, while the hyperbranched polymer has an
5   irregularly repeated branching structure. These polymers may
have a structure in which the polymer chains are
dendritically branched from one focal point, or a structure
in which polymer chains are radiated from a plurality of
focal points linked to a polyfunctional molecule serving as a
10   core. Although other definitions of these species may also
be acceptable, in any case, the dendritic polymer of the
present invention encompasses dendritic polymers having a
regularly repeated branching structure and those having an
irregularly repeated branching structure, wherein these two
15   types of dendritic polymers may have a dendritically
branching structure or a radially branching structure.

According to a generally accepted definition, when a
dendritic structural unit extends from its preceding
dendritic structural unit as an exact copy thereof, the
20   extension of the unit is referred to as the subsequent
"generation." It should be noted that the definition of a
"dendritic polymer" according to the present invention covers
those having a structure in which each of the dendritic
structural units which are similar to one another with the
25   same basic structure are repeated at least once also fall
within the scope of the present invention.

The concepts in relation to dendritic polymer,

dendrimer, hyperbranched polymer, etc. are described in, for example, Masaaki KAKIMOTO, Chemistry, Vol. 50, p. 608 (1995) and Kobunshi(High Polymers,Japan), Vol. 47, p. 804 (1998), and these publications can be referred to and are

5   incorporated herein by reference. However, the descriptions in these publications should not be construed as limiting the present invention thereto.
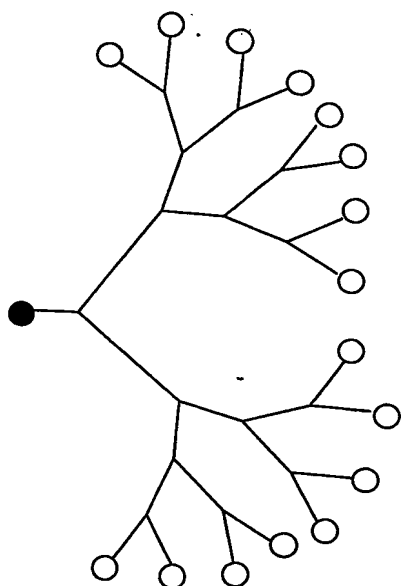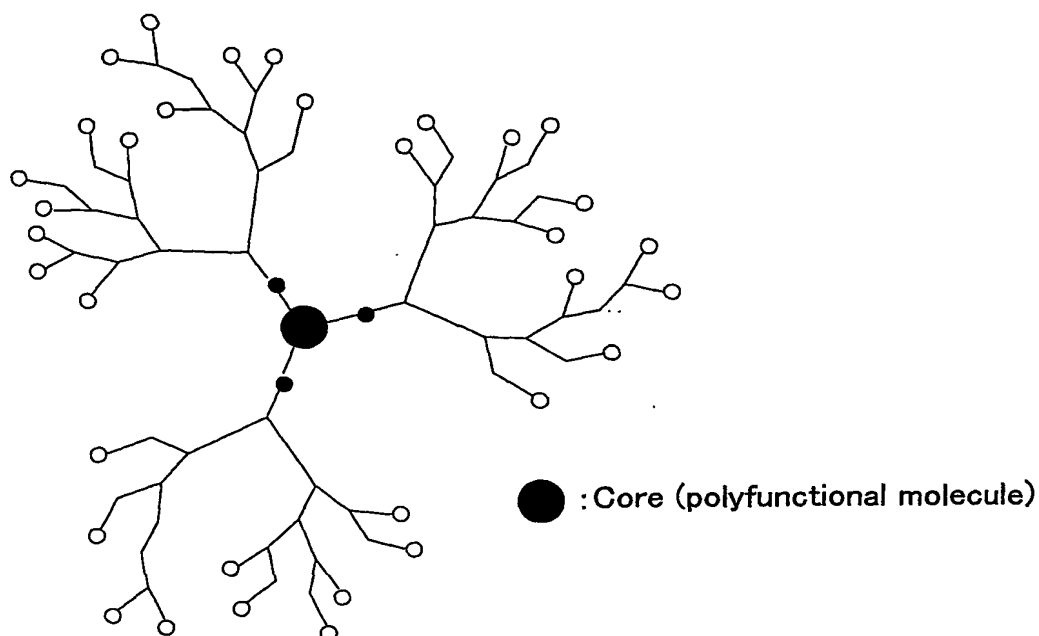
Dendrimer   **Hyperbranched polymer**

● :Focal point
○ :End

● : Core (polyfunctional molecule)
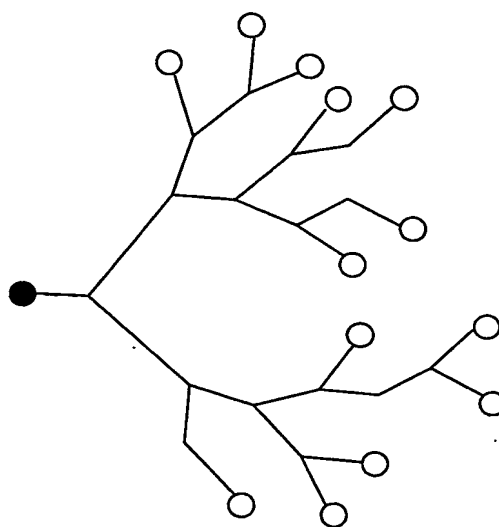
In the dendritic polymer of the present invention, a dendritic structural unit is formed of a linear portion X and a branch portion Y. The structure in which the dendritic structural unit is repeated once to provide a two-stage

5   structure is in fact "a structure in which each of the branch portions Y of that structural unit is bonded to another but identical structural unit." The resultant structure is referred to as a "1st-generation dendron." A similar structure in which dendritic units having the same structure

10   are successively linked to the bonding hands of the branch portions Y of a 1st-generation dendron is referred to as a "2nd-generation dendron. In a similar manner, an nth-generation dendron is created. Such dendrons *per se* and dendrons to which a desired substituent or substituents are

15   bonded to the ends or the focal point thereof are referred to as "dendrimers or hyperbranched polymers of dendritically

branching structure." When a plurality of dendritically branched dendrimers or hyperbranched polymers, which are identical to or different from one another, are bonded as subunits to a multivalent core, the formed dendritic polymer

5   is called "dendrimer or hyperbranched polymer of radially branching structure." Notably, a dendritic polymer in which nth-generation dendrons are linked to an r-valent core is defined as an nth-generation, r-branched dendrimer. Herein, a 1st-generation, 1-branched polymer in which the 1st-

10   generation dendron is bonded to the mono-valent core also falls within the scope of the dendritic polymer of the present invention. However, in order to attain the objects of the present invention, dendritic polymers of at least 1st-generation, 2-branched species or of at least 2nd-generation,

15   1-branched species are preferred. Generally, such dendritic polymers preferably have a molecular weight of 600 or more.

The dendritic polymer of the present invention has a structure in which the linear portion X contains at least one thienylene moiety and is at least partially conjugated with

20   the branch portion Y, and preferably has a linear portion X represented by formula (3). Therefore, the dendritic polymer provides an organic semiconductor material which is isotropic and which exhibits remarkably high carrier conductivity.

As used herein, the expression "at least partially

25   conjugated with" refers not only to the case where a perfect conjugated system is established, but also to the case where not all the electrons of the π-electron systems are

ubiquitously present. For example, a conjugated system

containing an m-substituted benzene nucleus also falls within

the meaning of this definition.

    By virtue of such a structure, the dendritic polymer of

5   the present invention reversibly assumes an insulative state

and a metallic(conductive) state, depending on the presence

of an external factor. Generally, the external factor is

derived from electricity, photoexcitation, etc.

Electromagnetic excitation and mechanical outer force may

10 also be employed.

    Specifically, when an external factor is applied to the

dendritic polymer of the present invention, a polaron

state——an orbit or state differing in energy from a

bipolaron ——is attained, whereby a semiconducting

15 characteristic attributed to polaron hopping conduction is

expressed. In other words, when the dendritic polymer of the

present invention assumes a polaron state, a polaron orbit is

generated in a forbidden band included in the energy band of

the polymer. Although this phenomenon similarly occurs in

20 the case of bipolaron, the generated polaron state is

unstable. Therefore, the polaron state is maintained during

application of an external factor, but is broken out or is

not formed in the presence of a weak external factor or in

the absence of the external factor.

25 Accordingly, the dendritic polymer of the present

invention assumes either an insulative state or a conductive

state, depending on the presence of such an external factor;

i.e., exhibits semiconducting characteristics. Although application of the external factor possibly leads to an insulative state or a metallic state, the conductive state is generally attained through application of the external factor.

5   Herein, the term "insulative state" refers to a state of insulation involving a band gap (forbidden band width) of, for example, approximately 2.5 eV. The term " metallic (conductive) state" refers to a state of conduction involving a band gap (forbidden band width) between the valence

10 electron band and the lower-energy polaron band of, for example, approximately 0.4 eV.

The dendritic polymer of the present invention exhibits the aforementioned semiconducting characteristics even when it contains no substantial doping reagent. However, the

15 dendritic polymer may be doped with a certain dopant to thereby stabilize semiconducting characteristics or may be doped to thereby express semiconducting characteristics.

Examples of the doping reagent include n-type or p-type dopants generally employed in conductive polymers. Specific

20 examples include alkali metals, alkylammonium ions, halogens, Lewis acids, protic acids, and transition metal halides. In addition, dopants described in " Kobunshi Electronics(Polymer Electronics,Japan)," published by Corona, p. 32 and those described in " Dodensei Kobunshi No Kiso To Oyo(Base and

25 Applications Conductive Polymers,Japan)," published by IPC, p. 24 may also be employed.

Notably, the dendritic polymer employed in the present

invention may be endowed, on the molecular surface, with hole conductivity, electron conductivity, or ion conductivity so as to enhance the aforementioned semiconducting properties and carrier conductivity.

5   No particular limitation is imposed on the structure of the dendritic polymer of the present invention, so long as the linear portion X contains at least one thienylene moiety and is at least partially conjugated with the branch portion Y. However, since an object of the invention is to attain

10   high carrier conductivity, the portion X preferably has a structure represented by formula (3).

The substituent Z in the above formula is a single bond or an optionally substituted divalent organic group which is at least partially conjugated with thienylene. For example,

15   the substituent Z is a substituent formed from a moiety selected from the group consisting of substituted or unsubstituted chain hydrocarbon (aliphatic hydrocarbon) moieties, substituted or unsubstituted cyclic hydrocarbon (including alicyclic compound and aromatic compound) moieties,

20   and substituted or unsubstituted heterocyclic compound (including aromatic heterocyclic compound and non-aromatic heterocyclic compound) moieties; a substituent formed from a plurality of same moieties continuously linked together selected from said group; or a substituent formed from a

25   plurality of different moieties continuously linked together selected from said group. Each of these component moieties is at least partially conjugated with another component

21

moiety.   Each of R_4 and R_5, which may be different from each
other, represents a hydrogen atom, an alkyl group, or an
alkoxy group. · In the present specification, unless otherwise
specified, groups such as an alkyl group and an alkoxy group
5   have 1 to 20 carbon atoms.

Preferably, the substituent Z is a substituent formed
from a moiety selected from the group consisting of
substituted or unsubstituted unsaturated aliphatic
hydrocarbon moieties and substituted or unsubstituted cyclic
10   or heterocyclic aromatic compound moieties; a substituent
formed from a plurality of same moieties continuously linked
together selected from said group; or a substituent formed
from a plurality of different moieties continuously linked
together selected from said group. More preferably, the
15   substituent Z is a substituent formed from a moiety selected
from the group represented by formula (4); a substituent
formed from a plurality of same moieties continuously linked
together selected from said group; or a substituent formed
from a plurality of different moieties continuously linked
20   together selected from said group.

Specific examples of preferred groups which can be used
as the linear portion X include, but are not limited to, the
groups represented by the following formula (6).

(6)
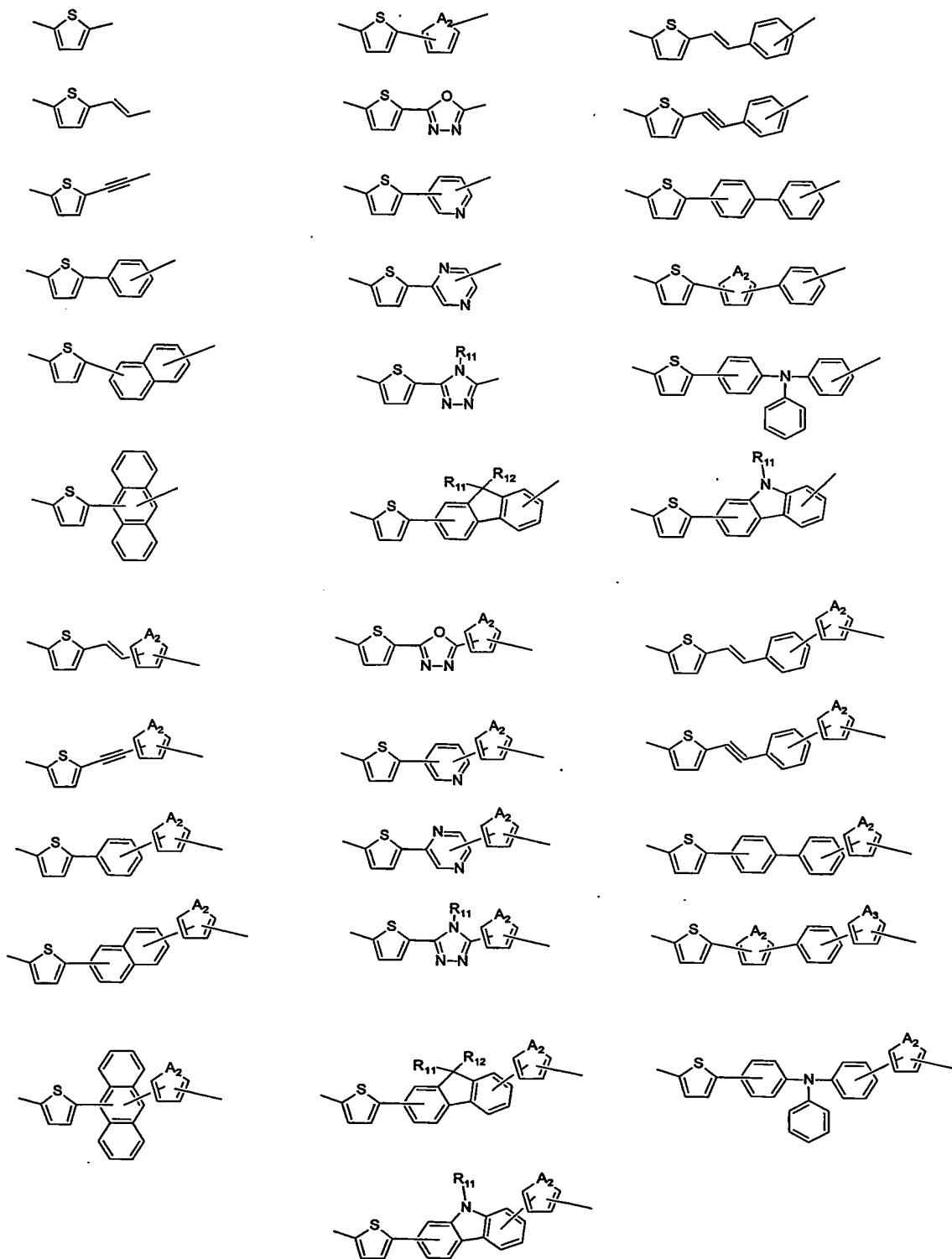
A_2, A_3 = O, S, $N-R_{13}$

R_{11}, R_{12}, R_{13} = a hydrogen atom, an alkyl group

No particular limitation is imposed on the structure of
5   the branch portion Y of the dendritic polymer of the present
invention, so long as the portion Y is a trivalent organic
group and is at least partially conjugated at least with the
linear portion X.   However, the branch portion Y preferably
includes, as a branching center, a chemical entity selected
10   from among chain hydrocarbons (aliphatic hydrocarbons),
cyclic hydrocarbons (including alicyclic compounds and
aromatic compounds), and heterocyclic compounds (including
aromatic heterocyclic compounds and non-aromatic heterocyclic
compounds).

15   The entirety of the branch portion Y may be a trivalent
organic group formed from a moiety selected from the group
consisting of substituted or unsubstituted chain hydrocarbon
moieties, substituted or unsubstituted cyclic hydrocarbon
moieties, and substituted or unsubstituted heterocyclic
20   compound moieties; a trivalent organic group formed from a
plurality of same moieties continuously linked together
selected from said group; or a trivalent organic group formed
from a plurality of different moieties continuously linked
together selected from said group.   Each of these component
25   moieties is at least partially conjugated with another
component moiety.

Examples of preferred branch portions Y include, but

are not limited to, a structure represented by formula (2).

In one particularly preferred embodiment of the dendritic polymer of the present invention, the repeating unit represented by formula (1) has a structure represented

5　by the aforementioned formula (5), wherein n is an integer of 1 to 10, preferably 1 to 3.

In the dendritic polymer of the present invention, a center moiety serving as a core may be bonded to the portion X in the repeating unit at starting point of a branching

10　structure. Briefly, the core can be linked to arbitrary numbers of starting points of a dendritically branching structure, and refers to a partial structure other than a branching structure. In other word, the core serves as the center of dendritic polymer molecules, and refers to a

15　portion of a dendritic polymer other than repeating units.

The core is preferably formed of a group which has a valence of at least 2 and to which two or more repeating units can be directly bonded. Specific examples include C1-C20 alkylene groups, C6-C20 arylene groups, and groups in

20　which these alkylene groups and arylene groups are combined. In addition to unsubstituted alkylene groups, the alkylene groups may contain therein a heteroatom such as O, NH, N(CH$_3$), S, or SO$_2$, or may have a substituent such as a hydroxyl group, a carboxyl group, an acyl group or a halogen (e.g., fluorine,

25　chlorine, bromine, or iodine) atom. The core may be a multivalent group of any of the above described groups from which a hydrogen atom bonded to a carbon atom is removed; a

multivalent heterocyclic group; a group in which the heterocyclic group and any of the above hydrocarbon group are bonded together; a porphyrin; or a porphyrin complex. In addition to the examples of cores having a valence of at

5   least two, a monovalent core formed by bonding hydrogen atom(s) to a multivalent core may also be used.

In the dendritic polymer of the present invention, the portion Y included in a repeating unit and serving as an end of the branching structure may be bonded to end moieties,

10 which are different from the repeating unit. The expression "end moieties" is used to refer to a surface structure in which arbitrary numbers of ends of a dendritically or radially branching structure are bonded thereto to thereby form a molecular surface of the dendritic polymer (i.e., a

15 partial structure excluding the dendritic or radial branches (repeating units)). No particular limitation is imposed on the structure of the end moieties of the dendritic polymer of the present invention, and moieties having hole conductivity, electron conductivity, or ion conductivity are preferably

20 used in order to attain high carrier conductivity. Specific examples of end moieties include, but are not limited to, those represented by the following formula (7). No particular limitation is imposed on the mode of bonding between these end moieties and dendritic structural units,

25 and examples thereof include carbon-carbon bond, carbon-nitrogen bond, amido bond, ether bond, ester bond, and urea bond.

(7)
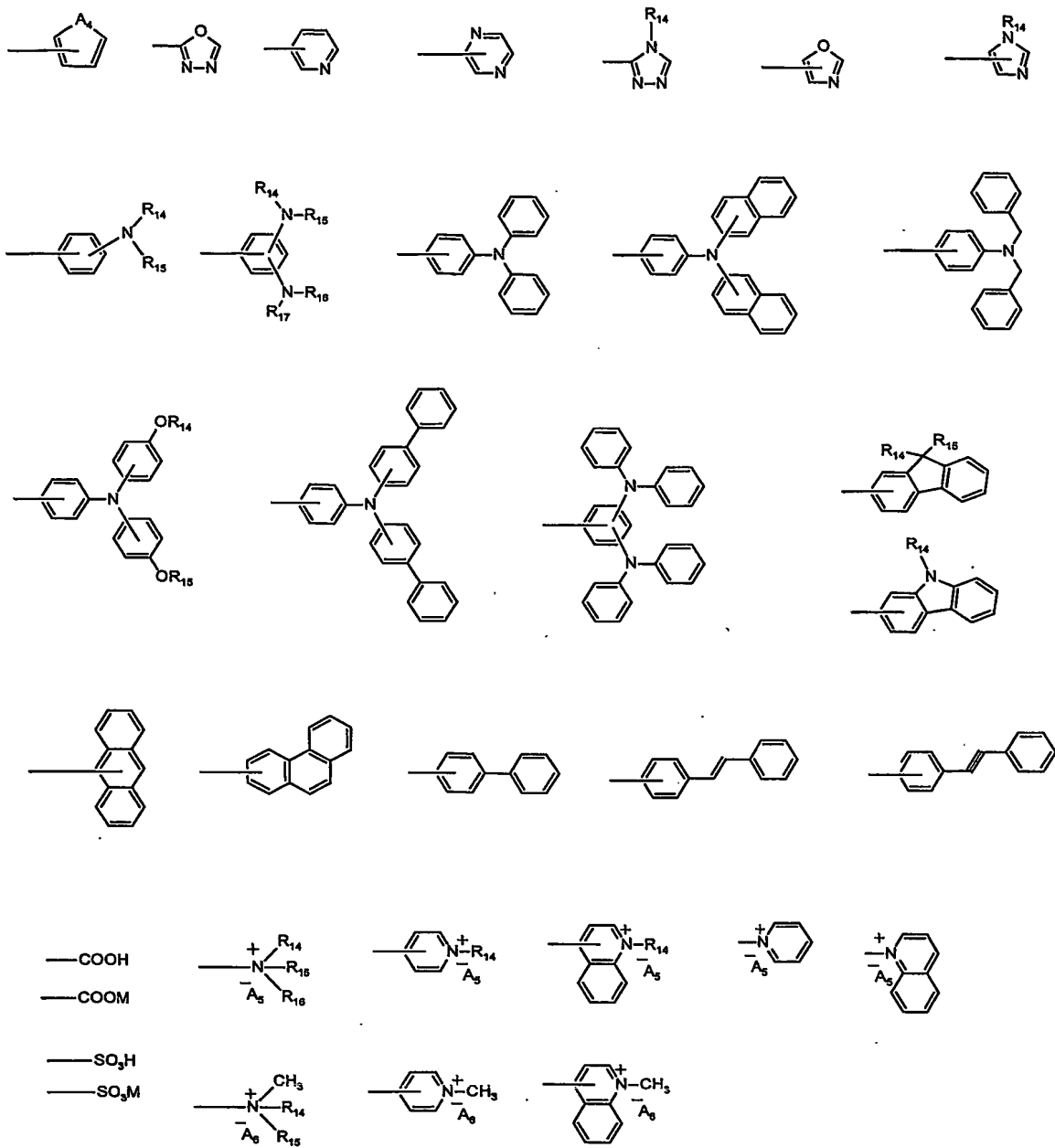
A_4 = O, S, N–R_18

R_14 to R_18 = a hydrogen atom or an alkyl group

A_5 = Cl, Br, I

A_6 = CH_3SO_4

M = Li, Na, K, ammonium, monoalkylammonium, dialkylammonium,

trialkylammonium, or tetraalkylammonium

Notably, dendritic polymers having no core(s) or end
moieties also fall within the scope of the present invention.
5   In this case, the starting point and end moieties of the
branching structure of the dendritic polymer of the present
invention are determined in accordance with the starting
material for producing repeating units forming the branching
structure. At starting point or end moieties of the
10 branching structure, active groups of starting material may
be substituted by hydrogen.

No particular limitation is imposed on the branching
structure of the dendritic polymer of the present invention
so long as the polymer has a dendritic structure, and the
15 dendritic polymer does not necessarily have a completely
ordered branching structure (i.e., dendrimer). No particular
limitation is imposed on the number of generations of the
dendritic polymer. The term "generation of dendritic
polymer" refers to the expression described above. The
20 number of generations of dendritic polymers including those
having a large or long center moiety is generally 1 to 10.
However, the number is preferably 1 to 8, more preferably 1
to 7, most preferably 2 to 5, from the viewpoint of spatial
density of end moieties and easiness of synthesis.

25 As described above, the dendritic polymer of the
present invention having a large number of branches provides
a large number of branch ends. Through employment of the

28

ends, the number of carriers can be increased.

Furthermore, since the dendritic polymer provides a
large number of paths for carrier conduction, carrier
mobility can be effectively enhanced without orienting
5   molecules and increasing crystallinity, which have been
performed for conventional conjugated polymers and low-
molecule organic semiconductor materials.

The dendritic polymer of the present invention can be
formed (i.e., synthesized) from a monomer containing a
10   thienylene structure. As used herein, the term "monomer"
refers to a class of low-molecular-weight compounds having a
partial structure represented by formula (1), the compounds
including derivatives thereof to which mutually reactive
substituents are introduced, and precursors thereof. No
15   particular limitation is imposed on the synthesis method for
forming a dendritic polymer structure from a mononer, and
methods which may be employed include the "divergent method"
in which branches are successively extended from a focal
point; the "convergent method" in which branches are extended
20   from branch ends and the thus-connected units are finally
bonded to a focal point; and polycondensation of a
polyfunctional monomer of AB_2 type (A and B are mutually
reactive functional groups). Among these methods, the
"convergent method" is preferred for effectively synthesizing
25   a high-purity dendritic polymer having no defects, from the
viewpoint of no requirement for excessive amounts of starting
materials and easiness of purification of products.

For example, a dendritic polymer having a structural
repeating unit represented by formula (8) can be produced
through the "convergent method" including reaction steps
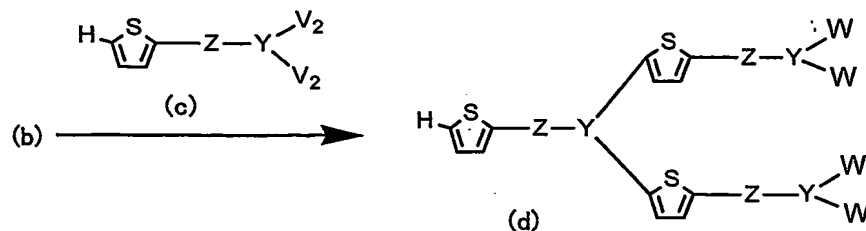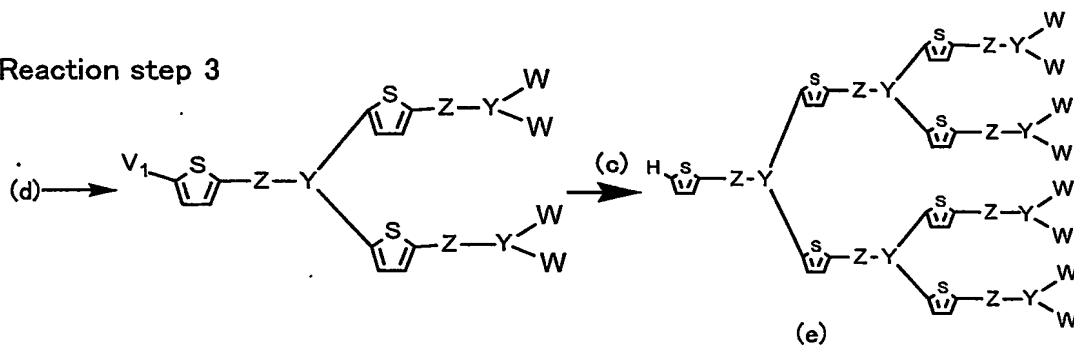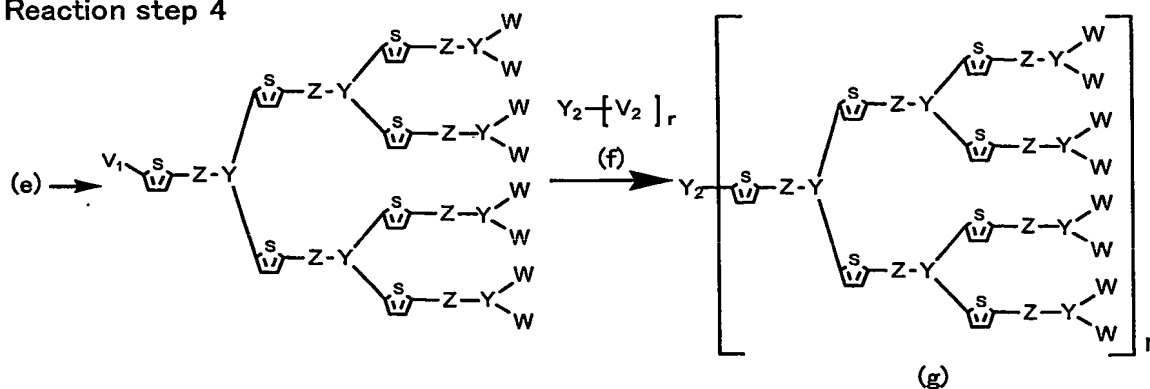represented by scheme (9).

                    (8)

5
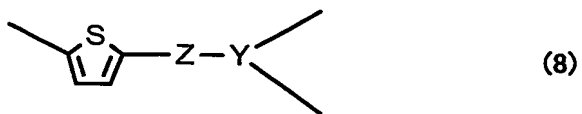
(9)

Reaction step 1

Reaction step 2

Reaction step 3

Reaction step 4

The reaction steps represented by scheme (9) include reaction step 1 in which α hydrogen of the thiophene ring of compound (a) for forming end moieties is converted to active

group V_1, to thereby form compound (b); reaction step 2 in
which compound (c) having a linear portion and a branch
portion and two active groups V_2 at the branch portion is
reacted with the compound (b), to thereby yield compound (d);
5 and reaction step 3 in which α hydrogen of the thiophene
ring of the obtained compound (d) is converted to active
group V_1, and the compound (c) is reacted with V_1, to thereby
form a dendron (e) of a subsequent generation. In addition,
when the dendron is bonded to a center moiety molecule, there
10 is carried out reaction step 4 in which α hydrogen of the
thiophene ring of the compound (e) is converted to active
group V_1, and compound (f) for forming a center moiety is
reacted with V_1, to thereby form compound (g).

In the reaction scheme (9), each of V_1 and V_2 represents
15 an active group, and W represents a monovalent organic group
containing no active group which optionally has a substituent.
The expression "containing no active group" means that a
group which is reactive to V_1 or V_2 is not included.

Y_2 represents an r-valent organic group (r is an integer
20 of ≥ 1) serving as a core. The "r" of compound (g) refers to
the number of branches generating from the center moiety.
When nth-generation dendrons are bonded to a core having r of
two or more, an nth-generation, r-branched dendritic polymer
of a radially branching structure is obtained. When r is 1,
25 a dendritic polymer of a dendritically branching structure is
formed. In the present invention, Y_2 of this type of
dendritic polymer is also referred to as a "core."

Among the above mentioned compounds, compound (d) can be called a 1st-generation dendrimer, whereas compound (e) can be called a 2nd-generation dendrimer. For the purpose of simple description, only denderimers of the number of

5   generations 1 and 2 are shown in the aforementioned reaction steps 1 to 3 in scheme (9). However, dendrimers of further generations can be produced by repeating reaction step 3.

In reaction step 4, the dendrimer obtained in reaction step 3 can be bonded to a compound which can serve as a

10   center moiety. In the above scheme, 2nd-generation dendrimers (e) are bonded to compound (f) serving as a center moiety. However, dendrimers of any generation can be bonded to a center structure molecule according to a similar reaction step. However, as also mentioned above, the number

15   of generations of dendrimers is preferably 1 to 8, more preferably 1 to 7, most preferably 2 to 5, and the number of branches from the center moiety is preferably 1 to 6, more preferably 1 to 4, from the viewpoint of spatial density of dendritic structural units and easiness of synthesis.

20   No particular limitation is imposed on the method of synthesizing compound (a) serving as a starting material in reaction step 1. The compound (a) can be produced according to the following reaction scheme (10) in which W for forming end moieties is bonded to Y through reaction with V_1 and V_2.

33

(10)

(a)
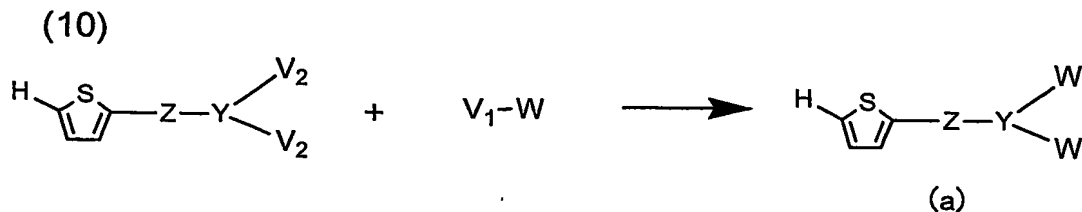
In the reaction schemes (9) and (10), dendritic polymers having an end portion in which the portion Y are bonded to two W groups are shown. However, a structure in which one W is bonded to Y or a structure in which no W is bonded to Y is also acceptable. Furthermore, Y is an organic group other than those described above. In this case, a 1st-generation dendritic polymer is synthesized in reaction step 3.

When tertiary aromatic amine skeletons ——hole conductive material——are introduced to branch ends, in one possible approach, a trivalent aromatic group such as benzene nucleus is employed as Y, and nitrogen atoms are bonded directly to the nucleus. Specifically, when the compound in which V_2 is a halogen and V_1-W is a secondary aromatic amine compound represented by the following formula is employed in reaction scheme (10), the above tertiary aromatic amine skeletons can be synthesized through condensation reaction.
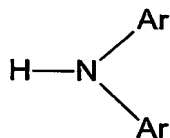
Ar: a monovalent aromatic group

Examples of the monovalent or trivalent aromatic group

include substituted or unsubstituted aromatic hydrocarbon
groups, aromatic heterocyclic groups, condensed polycyclic
aromatic hydrocarbon groups, condensed heterocyclic aromatic
groups, and monovalent or trivalent aromatic groups formed
5   through ring-condensation of these groups. Specific examples
include benzene, naphthalene, anthracene, naphthacene,
pentacene, hexacene, phenanthrene, phenalene, pyrene,
chrysene, benzoanthracene, perylene, triphenylene, coronene,
pentaphene, picene, naphthoanthracene, trinaphthylene,
10   ovalene, biphenyl, terphenyl, quaterphenyl, quinquphenyl,
sexiphenyl, septiphenyl, phenylanthracene, phenylnaphthalene,
diphenylanthracene, biphenylene, binaphthalenyl, fluorene,
acenaphthylene, dibenzoperylene, indene, pentalene,
acephenanthrylene, indacene, aceanthrylene, tetraphenylene,
15   fluoranthene, azulene, cyclooctatetraene, octarene, rubrene,
thiophene, furan, pyrrole, silole, oxazole, thiazole,
imidazole, pyrazole, furazane, oxadiazole, thiadiazole,
pyridine, thiopyran, pyrimidine, pyrazine, pyridazine,
triazine, benzothiophene, benzofuran, benzosilole, indole,
20   benzoxazole, benzothiazole, benzimidazole, quinoline,
thiochromene, quinazoline, carbazole, dibenzosilole,
dibenzofuran, dibenzothiophene, phenanthroline, acridine,
benzoquinoline, phenanthridine, phenazine, phenothiazine,
thianthrene, phenoxathiine, phenoxazine, bithiophene,
25   terthiophene, quaterthiophene, bifuran, terfuran, quaterfuran,
bipyrrole, terpyrrole, quaterpyrrole, bisilole, tersilole,
quatersilole, bipyridine, terpyridine, quaterpyridine,

phenylpyrrole, phenylpyridine, phenylfuran, phenylthiophene, and phenyloxadiazole. These groups may serve as monovalent aromatic groups or trivalent aromatic groups and may be substituted or unsubstituted.

5   The condensation reaction can be performed through, for example, Ullmann condensation (see Chem. Lett., 1145, (1989), Synth. Commu. 383, (1987), etc.) employing copper and a base catalyst, or the Toso method (Japanese Patent Application Laid-Open (*kokai*) No. 10-310561) employing a palladium

10 catalyst-tri-t-butylphosphine ligand and a base catalyst. Of these, the Toso method is preferred, since reaction can be performed under mild conditions and high yield and selectivity can be attained. Through employment of the reaction, tertiary aromatic amine skeletons are introduced

15 through, for example, the following reaction scheme.
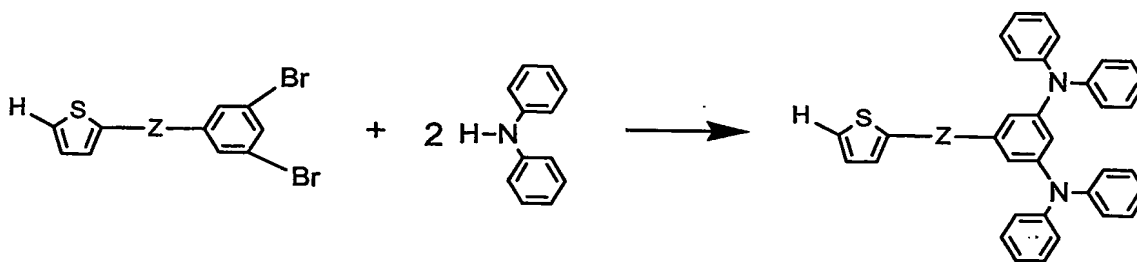
Specific reactions, conditions, etc. will next be described in more detail.

Reaction of V_1 and V_2 with compound (c) in reaction step 2 or 3 is suitably performed through cross-coupling reaction such as Suzuki cross-coupling. Examples of combinations of active groups V_1 and V_2 (V_1, V_2) include (a group selected from Group 1, a group selected from Group 2) and (a group

selected from Group 3, a group selected from Group 4).

Group 1

—$B(OH)_2$

—$B(OR)_2$.
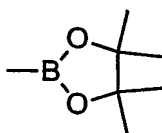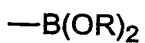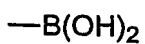
R = methyl, ethyl, isopropyl, butyl

Group 2

Cl, Br, I, OSO_2 (C_kF_{2k+1})
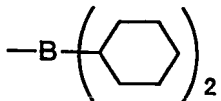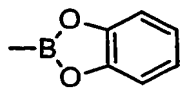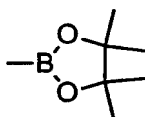
$k=1, 4$

Group 3

Cl, Br, I

Group 4

—$B(OH)_2$

—$B(OR)_2$
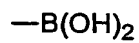
R = methyl, ethyl, isopropyl, butyl
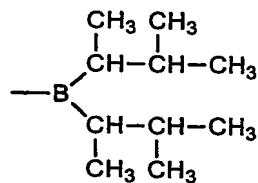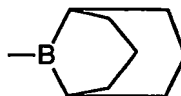
5   Suzuki cross-coupling reaction is known to impose few
limitations on functional groups to be employed, to provide
high selectivity of reaction, and to cause few side reactions

such as homo-coupling, and is particularly employed for a
wide range of cross-coupling reactions of aromatic compounds
and vinyl compound derivatives (see Suzuki et al., Yuki Gosei
Kagaku Kyokai Shi (Journal of Synthetic Organic Chemistry,
Japan), 46, 848, (1988), Suzuki et al., Chem. Rev., 95, 2457
(1995), and Suzuki, J. Organomet. Chem., 576, 147 (1999)).
Combinations of V_1 (boric acid ester; $B(OH)_2$ or $B(OR)_2$) and V_2
(Br or I) are preferably employed, from the viewpoint of high
yield and selectivity, applicability, etc.

Suzuki cross-coupling reaction conditions under which
conversion of α hydrogen of the thiophene ring to active
group V_1 and reaction of active groups V_1 and V_2 are performed
will next be described.

[Conversion of α hydrogen of the thiophene ring to active
group V_1]

Reaction conditions employed in reaction steps 1 and 3
for converting α hydrogen of the thiophene ring to active
group V_1 selected from Group 1 will be described.

When V_1 is formed from $B(OR)_2$ or the boric acid ester
represented by the following formula, α hydrogen of the
thiophene ring is drawn through the action of alkyllithium
(e.g., n-butyllithium), lithium diisopropylamide, etc., to
thereby form the corresponding carbanion, and subsequently,
the corresponding alkoxyborane (i.e., trimethoxyborane,
triethoxyborane, triisopropoxyborane, tributoxyborane, or 2-
isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxabororane) is
electrophilically added to the carbanion.
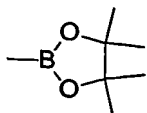
Examples of preferably employed solvents include organic solvents such as tetrahydrofuran, n-hexane, diethyl ether, and toluene. The reactions are preferably performed for 10 minutes to three hours at −100 to 30°C, more preferably for 30 minutes to two hours at −78 to 0°C.

When V_1 is formed from $B(OH)_2$, any of the boric acid esters obtained in the above manner is hydrolyzed through addition of water. Although no particular limitation is imposed on the reaction solvent, water is directly added to the reaction mixture yielded upon synthesis of a boric acid ester in the above manner, to thereby perform hydrolysis. The addition of water is convenient for production. The reaction is preferably performed for one hour to three hours at 0 to 50°C.

Reaction conditions employed in reaction steps 1 and 3 for converting α hydrogen of the thiophene ring to active group V_1 selected from the abovementioned Group 3 will be described.

When V_1 is formed from any of Cl, Br, and I, the corresponding halogenating reagent is reacted, to thereby convert α hydrogen of the thiophene ring to halogen. Examples of halogenating agents include N−chlorosuccinimide, N−bromosuccinimide, and N−iodosuccinimide. Examples of preferably employed reaction solvents include organic solvents such as tetrahydrofuran, n−hexane, diethyl ether,

benzene, carbon tetrachloride, carbon disulfide,

dimethylformamide, and acetic acid. The reaction is

preferably performed for one hour to 24 hours at -20 to 80°C.

[Reaction of active group V_1 and active group V_2]

5   Reaction conditions employed in reaction steps 2 and 3

for reacting V_1 and V_2 through Suzuki cross-coupling will be

described.

When Suzuki cross-coupling is performed, a variety of

combinations of palladium catalysts and base catalysts can be

10   employed.

Examples of palladium catalysts include

tetrakis(triphenylphosphine)palladium, palladium acetate,

palladium chloride, palladium black,

bis(triphenylphosphine)palladium dichloride, bis(tri-o-

15   tosylphosphine)palladium dichloride,

bis(dibenzylideneacetone)palladium,

bis(tricyclohexylphosphine)palladium dichloride,

bis(triphenylphosphine)palladium diacetate, [1,2-

bis(diphenylphosphino)butane]palladium dichloride, and [1,2-

20   bis(diphenylphosphino)ethane]palladium dichloride. In

addition, combination of a ligand compound with these

palladium catalysts may be effective. Examples of ligand

compounds include triphenylphosphine, 1,1'-

bis(diphenylphosphino)ferrocene, 1,2-

25   bis(diphenylphosphino)ethane, 1,3-

bis(diphenylphosphino)propane, 1,4-

bis(diphenylphosphino)butane, sodium

diphenylphosphinobenzene-3-sulfonate, tricyclohexylphosphine, tri(2-furyl)phosphine, tris(2,6-dimethoxyphenyl)phosphine, tris(4-methoxyphenyl)phosphine, tris(4-methylphenyl)phosphine, tris(3-methylphenyl)phosphine, and tris(2-

5 methylphenyl)phosphine. Instead of palladium catalysts, a nickel catalyst, [1,1'-bis(diphenylphosphino)ferrocene]nickel dichloride may also be used.

Examples of base catalysts include sodium carbonate, sodium alkoxides (e.g., sodium ethoxide), t-butoxypotassium,

10 barium hydroxide, triethylamine, potassium phosphate, sodium hydroxide, and potassium carbonate.

When Suzuki cross-coupling is performed, any of a variety of organic solvents, mixtures thereof, and mixtures thereof with water is generally used as a solvent. Examples

15 of suitably used organic solvents include dimethylformamide, ethanol, methanol, dimethyl sulfoxide, dioxane, benzene, toluene, tetrahydrofuran, dimethoxyethane, dimethylacetamide, and xylene. The coupling reaction is performed preferably for 30 minutes to 24 hours at 25 to 150°C, more preferably

20 for one hour to 12 hours at 25 to 80°C.

In reaction step 4 and scheme (10), conversion of α hydrogen of the thiophene ring to active group V_1 and reaction of V_1 and V_2 are performed in a manner similar to that employed in reaction steps 1 to 3.

25 The compound yielded in each reaction step is purified, whereby a high-purity dendritic polymer having few defects is synthesized. No particular limitation is imposed on the

41

purification method, and purification methods such as
recrystallization, crystallization, sublimation, and
purification by means of a column may be employed.

According to the aforementioned production method, a
variety of dendritic polymers can be produced by selecting
species of compound (a) for forming branch ends, compound (c)
serving as a monomer for forming a dendritic structure, and
compound (f) for forming a center moiety. Since the
production method is based on the "convergent method," in
which a purification process in each reaction step is readily
performed, a high-purity dendrimer (a type of dendritic
polymer) having few defects can be produced.

The dendritic polymer of the present invention, having
carrier conductivity, is envisaged to be used in a variety of
fields. The dendritic polymer of the present invention can
provide hole-transporting (p-type), electron-transporting (n-
type), and a variety of functional electronic materials, by
selecting the molecular structure thereof or by doping or a
similar process. Thus, such electronic materials can be used
in switching elements such as an organic transistor element,
an organic FET element, or an organic TFT element; solar
cells; photoelectric conversion elements; capacitors; light-
emitting elements; electrochromic elements; polymer secondary
batteries, etc. The structure of such elements suited for
each purpose will next be described in detail.

The organic transistor element includes a semiconductor
layer formed of an organic layer having hole transportability

and/or electron transportability; a gate electrode formed of
a conductive layer; and an insulating layer inserted between
the semiconductor layer and the conductive layer. To the
assembly, a source electrode and a drain electrode are

5   attached, to thereby produce the transistor element. The
above organic layer is formed from the dendritic polymer of
the present invention.

The light-emitting device includes a pair of plate-like
electrodes disposed in parallel, and an organic layer

10 containing the material of the present invention between the
two electrodes. Generally, the device is formed of a
transparent electrode (e.g., ITO), a hole-injecting layer, a
hole-transporting layer, a light-emitting layer, an electron-
transporting layer, and a metal electrode. Carrier-

15 transporting function and light-emitting function may be
combined in a single structure. The above organic layer is
formed from the dendritic polymer of the present invention.

The photoelectric conversion element or a solar cell
generally contains an organic layer sandwiched by plate-like

20 electrodes disposed in parallel. The organic layer may be
formed on a comb-like electrode. No particular limitation is
imposed on the location of the organic layer. No particular
limitation is imposed on the material of electrodes. However,
when plate-like electrodes disposed in parallel are employed,

25 at least one electrode is preferably formed of a transparent
electrode such as an ITO electrode or a fluorine-doped tin
oxide electrode. The organic layer is formed of two sub-

layers; i.e., a layer formed of the dendritic polymer of the present invention having p-type semiconductivity or hole-transportability, and a layer formed of the dendritic polymer of the present invention having n-type semiconductivity or electron-transportability. Furthermore, when a photosensitizing dye group is introduced to the dendritic polymer contained in one of the two layers, or a polymer or hyperbranched polymer in a broad sense including a specific photosensitizing dye molecule moiety is provided between the two layers, element performance is further enhanced, and high-efficiency power generation can be attained by use of, for example, a solar cell of such a structure. Herein, the photosensitizing dye molecule moiety has a HOMO (highest occupied molecular orbital) level lower than the HOMO level of hole-transporting dendritic polymer and has a LUMO (lowest unoccupied molecular orbital) level higher than the LUMO level of electron-transporting dendritic polymer.

When an ion-conductive polymer or a dendritic polymer which satisfies conditions of photoexcitation of the hole-transporting layer or the electron-transporting layer is provided between the hole-transporting layer and the electron-transporting layer, an electrochemical photoelectric conversion element can be formed. A photosensitizing dye group may be introduced to any one of the layers in accordance with needs.

The capacitor includes a hole-transporting layer and an electron-transporting layer, one serving as a conductive

layer and the other serving as a semiconductor layer, and an
insulating layer inserted between the conductive layer and
the semiconductor layer. Alternatively, both the hole-
transporting layer and electron-transporting layer are formed

5   of conductive layers, and an ion-conductive layer is inserted
between the two conductive layers. Alternatively, the hole-
transporting layer is formed of a p-type semiconductor layer
and the electron-transporting layer is formed of an n-type
semiconductor layer, and the layers may be stacked, to

10 thereby form a continuously stacked multi-layer. The above
semiconductor layer is formed from the dendritic polymer of
the present invention.

The electrochromic element includes a hole-transporting
layer formed of a polymer layer which can be doped with a p-

15 type dopant and discolors by redox reaction; an electron-
transporting layer formed of a polymer layer which can be
doped with an n-type dopant and discolors by redox reaction;
and a layer containing a supporting electrolyte and disposed
between the two layers. The element structure may be used in

20 a polymer secondary battery, whereby a secondary battery of
high capacitance and low internal resistance is provided.

As described above, by use of the aforementioned
materials according to the present invention, devices
requiring carrier conductivity and having remarkably high

25 carrier conductivity can be produced through a simple
production process.

Examples

The present invention will next be described with reference to the below-described Examples in relation to the dendritic polymer and the function element using the same, which should not be construed as limiting the invention thereto. Apparatus, etc. employed in measurement are as follows.

^{1}H-NMR: FT-NMR, model JNM-AL400 (400 MHz, product of JEOL), solvent: CDCl$_3$ or DMSO-d^6, room temperature, chemical shift reference (0 ppm): tetramethylsilane (TMS).

GPC: HLC-8220 GPC, product of Tosoh Corporation; Column: TSK gel Super HZM-M; Eluent: THF; Detector: UV 254 nm; Measures (weight average molecular weight (Mw), number average molecular weight (Mn), and molecular weight distribution (Mw/Mn)) are reduced to polystyrene as a standard.

[Synthesis Example 1]   Synthesis of 3rd-generation dendritic polymer

<Synthesis Example 1-1>   Synthesis of a compound (c), 5-(3,5-dibromophenyl)-2,2'-bithiophene, serving as a monomer providing a dendritic structure, represented by the following formula
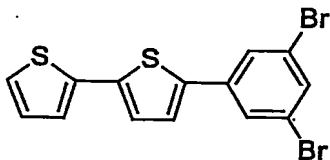
In a nitrogen atmosphere, 2,2'-bithiophene (4.6 g) was

dissolved in dehydrated tetrahydrofuran, and the solution was cooled in a dry ice – methanol bath. After cooling, a 1.6M n-butyllithium/hexane solution (18 mL) was added dropwise thereto, and the mixture was allowed to react for one hour.

5   Subsequently, trimethoxyborane (3.4 g) was added dropwise thereto, and the resultant mixture was allowed to react for one hour. After completion of reaction, water was added thereto for hydrolysis. Thereafter, the cooling bath was removed, whereby the temperature of the reaction mixture was

10   elevated to room temperature. An aqueous saturated ammonium chloride solution and diethyl ether were added to the reaction mixture, and the resultant mixture was stirred and left to stand. The formed organic layer was isolated from the mixture, and the aqueous layer was subjected to

15   extraction with a solvent mixture of tetrahydrofuran and diethyl ether (volume ratio: 1/2). The organic layer obtained through extraction was combined with the above organic layer, and the resultant mixture was washed with an aqueous saturated sodium chloride solution. The mixture was

20   dried over sodium sulfate, and the solvent was distilled off under reduced pressure, to thereby yield a crude product. The crude product was recrystallized from tetrahydrofuran/n-hexane, to thereby yield 4.3 g of 2,2!-bithiophene-5-boronic acid (intermediate compound; pale bluish white solid, yield:

25   73%) represented by the following formula.
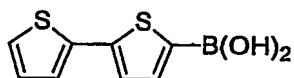
The structure of the obtained product was confirmed
through ¹H-NMR spectroscopy. The measurement data are shown
below.

¹H NMR (DMSO-d⁶) δ8.30 (s, BOH, 2H), δ7.60 (d, J=3.6 Hz,
thiophene ring, 1H), δ7.51 (dd, J=5.2 Hz, J=1.2 Hz, thiophene
ring, 1H), δ7.34-7.32 (m, thiophene ring, 2H), δ7.10 (dd,
J=5.2 Hz, J=3.6 Hz, thiophene ring, 1H).

Subsequently, in a nitrogen atmosphere, the resultant
intermediate compound, 2,2'-bithiophene-5-boronic acid (4.0
g) and 1,3,5-tribromobenzene (9.0 g) were dissolved in
tetrahydrofuran. Palladium acetate (0.1 g) and
triphenylphosphine (0.30 g) were added thereto, and a
solution of sodium carbonate (4.4 g) in water (34 mL) was
further added thereto. The mixture was allowed to react for
six hours while heating at 80°C in an oil bath under stirring.
After completion of reaction, the temperature of the reaction
mixture was lowered to room temperature, and water (30 mL)
was added thereto. The resultant mixture was subjected to
extraction with methylene chloride, and the formed organic
layer was washed with water. The organic layer was dried
over sodium sulfate, and the solvent was distilled off under
reduced pressure, to thereby yield a crude product. The
crude product was isolated and purified through column
chromatography (packing material: Silicagel 60 (product of

48

Merck), eluent: methylene chloride /n-hexane), to thereby yield 4.6 g of the target product (pale yellow solid, yield: 61%). The structure of the obtained product was confirmed through ^{1}H-NMR spectroscopy. The measurement data are shown below.

^{1}H NMR (CDCl$_3$) δ7.65 (d, J=1.6 Hz, benzene ring, 2H), δ7.55 (t, J=1.6 Hz, benzene ring, 1H), δ7.26-7.25 (thiophene ring, 1H), δ7.23 (d, J=3.6 Hz, thiophene ring, 1H), δ7.22 (d, J=3.6 Hz, thiophene ring, 1H), δ7.15 (d, J=3.6 Hz, thiophene ring, 1H), δ7.05 (dd, J=5.2 Hz, J=3.6 Hz, thiophene ring, 1H).

<Synthesis Example 1-2> Synthesis of a compound (a), 5-[2,2']bithiophenyl-5-yl-N,N,N',N'-tetraphenyl-1,3-phenylenediamine, forming the branch ends of a dendritic structure, represented by the following formula.


<Preparation of catalyst>
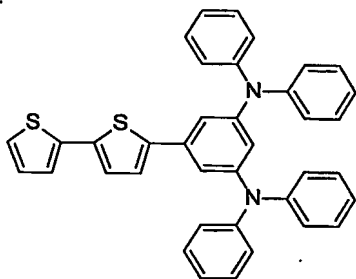
Xylene (4.5 mL) was added to palladium acetate (10 mg) and, in a nitrogen atmosphere, tri-t-butylphosphine (36 mg) was added thereto. The mixture was heated at 80°C for 30 minutes, to thereby prepare a catalyst solution.

<Synthesis of 5-[2,2']bithiophenyl-5-yl-N,N,N',N'-tetraphenyl-1,3-phenylenediamine>

Xylene (4.5 mL) was added to a mixture of 5-(3,5-
dibromophenyl)-2,2'-bithiophene (1.80 g) which had been
produced in Synthesis Example 1-1, diphenylamine (1.60 g) and
t-butoxypotassium (1.21 g), and, in a nitrogen atmosphere,

5   the previously prepared catalyst solution was added dropwise
thereto at 80°C. After completion of addition, the reaction
mixture was heated to 120°C, and was allowed to react for 18
hours. Subsequently, the temperature of the reaction mixture
was lowered to room temperature, and water (10 mL) was added

10   thereto. The formed organic layer was isolated from the
mixture, and the aqueous layer was subjected to extraction
with methylene chloride. The organic layer obtained through
extraction was combined with the above organic layer. The
organic layer was dried over sodium sulfate, and the solvent

15   was distilled off under reduced pressure, to thereby yield a
crude product. The crude product was isolated and purified
through column chromatography (packing material: Silicagel 60
(product of Merck), eluent: methylene chloride /n-hexane), to
thereby yield 2.20 g of the target product (pale yellow solid,

20   yield: 85%). The structure of the obtained product was
confirmed through ^{1}H-NMR spectroscopy. The measurement data
are shown below.

^{1}H NMR (CDCl$_3$) δ7.22 (t, J=7.8 Hz, benzene ring, 8H),
δ7.16 (dd, J=1.2 Hz, J=5.2 Hz, thiophene ring, 1H), δ7.11-

25   7.09 (m, thiophene ring, 1H and benzene ring, 8H), δ7.02-6.96
(m, benzene ring, 4H and thiophene ring, 3H), δ6.90 (d, J=2.0
Hz, benzene ring, 2H), δ6.73 (t, J=2.0 Hz, benzene ring, 1H).

<Synthesis Example 1-3> Synthesis of a compound (b), 5-(5'-boronic acid-[2,2']bithiophenyl-5-yl)-N,N,N',N'-tetraphenyl-1,3-phenylenediamine, represented by the following formula through conversion, to active group $B(OH)_2$, of α-hydrogen of the corresponding thiophene ring of compound (a) forming the branch ends of a dendritic structure
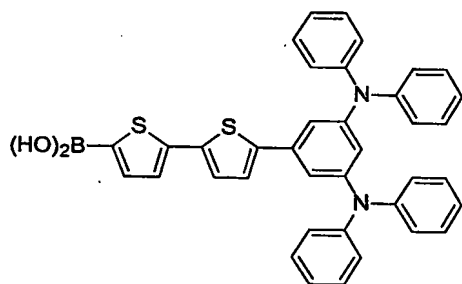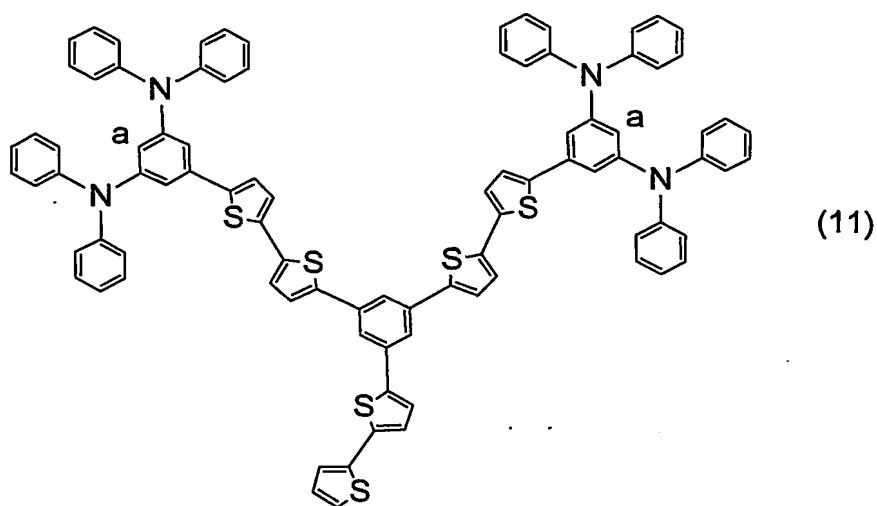

In a nitrogen atmosphere, 5-[2,2']bithiophenyl-5-yl-N,N,N',N'-tetraphenyl-1,3-phenylenediamine (2.0 g) which had been synthesized in Synthesis Example 1-2 was dissolved in dehydrated tetrahydrofuran, and the solution was cooled in a dry ice - methanol bath. After cooling, a 10-wt.% lithium diisopropylamide/n-hexane suspension (4.5 g, product of Aldrich) was added dropwise thereto, and the mixture was allowed to react for one hour. Subsequently, trimethoxyborane (0.5 g) was added dropwise thereto, and the resultant mixture was allowed to react for one hour. After completion of reaction, water was added thereto for hydrolysis. Thereafter, the cooling bath was removed, whereby the temperature of the reaction mixture was elevated to room temperature. An aqueous saturated ammonium chloride solution and diethyl ether were added to the reaction mixture, and the resultant mixture was stirred and left to stand. The

formed organic layer was isolated from the mixture, and the
aqueous layer was subjected to extraction with a solvent
mixture of tetrahydrofuran and diethyl ether (volume ratio:
1/2). The organic layer obtained through extraction was

5   combined with the above organic layer, and the resultant
mixture was washed with an aqueous saturated sodium chloride
solution. The mixture was dried over sodium sulfate, and the
solvent was distilled off under reduced pressure, to thereby
yield a crude product. The crude product was recrystallized

10   from tetrahydrofuran/n-hexane, to thereby yield 1.5 g of the
target product (pale yellow solid, yield: 70%). The
structure of the product was confirmed through ^{1}H-NMR
spectroscopy (solvent for measurement: DMSO-d^6) from the fact
that a peak attributed to the OH proton of the boronic acid

15   is observed at about 8.3 ppm and that the ratio of the
integrated value of the benzene-ring-originating protons to
that of the thiophene-ring-originating protons coincides with
that of the target structure product.

<Synthesis Example 1-4>   Synthesis of 1st-generation

20   dendritic polymer represented by the following formula (11)
through Suzuki cross-coupling reaction of compound (b) with
compound (c)

(11)

wherein, "a" represents the position of proton Ha, on which an integrated value obtained by ^{1}H-NMR spectroscopy was evaluated.

5   In a nitrogen atmosphere, THF (10 mL) and water (2 mL) were added to a mixture of 5-(5'-boronic acid-[2,2']bithiophenyl-5-yl)-N,N,N',N'-tetraphenyl-1,3-phenylenediamine (1.30 g) which had been produced in Synthesis Example 1-3; 5-(3,5-dibromophenyl)-2,2'-bithiophene

10   (0.40 g) which had been produced in Synthesis Example 1-1; palladium acetate (13 mg); triphenylphosphine (46 mg); and sodium carbonate (0.22 g), and the resultant mixture was allowed to react for eight hours under reflux conditions. After completion of reaction, the reaction mixture was cooled

15   to room temperature, and water (20 mL) was added thereto. The resultant mixture was subjected to extraction with methylene chloride, and the formed organic layer was washed with water. The organic layer was dried over sodium sulfate,

and the solvent was distilled off under reduced pressure, to

thereby yield a crude product. The crude product was

isolated and purified through column chromatography (packing

material: Silicagel 60 (product of Merck), eluent: methylene

5   chloride /n-hexane), to thereby yield 0.84 g of the target

product (pale yellow solid, yield: 60%). The structure of

the obtained product was confirmed through ^{1}H-NMR

spectroscopy (solvent for measurement: CDCl$_3$) with reference

to an integrated value at 6.74 ppm (2H) attributed to benzene

10   ring proton Ha (see formula (11)) having two adjacent

nitrogen atoms, from the fact that the ratio of the

integrated value of the benzene-ring-originating protons to

that of the thiophene-ring-originating protons coincides with

that of the target structure product. Hereinafter, in

15   descriptions in relation to other generations, Ha also refers

to a benzene ring proton having two adjacent nitrogen atoms.

The measurement data are shown below. The weight average

molecular weight (Mw), number average molecular weight (Mn),

and molecular weight distribution (Mw/Mn), as measured

20   through GPC were found to be 1,265, 1,241, and 1.019,

respectively. These values indicate that the target polymer

has high purity and assumes a single dispersion state.

^{1}H NMR (CDCl$_3$) δ7.66 (d, J=1.2 Hz, benzene ring, 2H),

δ7.65 (t, J=1.2 Hz, benzene ring, 1H), δ7.32 (d, J=3.6 Hz,

25   thiophene ring, 1H), δ7.30 (d, J=3.6 Hz, thiophene ring, 2H),

δ7.25-7.22 (m, benzene ring, 16H and thiophene ring, 2H),

δ7.18 (d, J=3.6 Hz, thiophene ring, 1H), δ7.13-7.10 (m,

54

benzene ring, 16H and thiophene ring, 2H), 7.08 (d, J=3.6 Hz,

thiophene ring, 2H), 7.05 (dd, J=5.2 Hz, J=3.6 Hz, thiophene

ring, 1H), 7.02-6.98 (m, benzene ring, 8H and thiophene ring,

2H), 6.92 (d, J=2.0 Hz, benzene ring, 4H), 6.74 (t, J=2.0 Hz,

5   benzene ring, 2H).

<Synthesis Example 1-5> Synthesis of 2nd-generation

dendritic polymer represented by the following formula
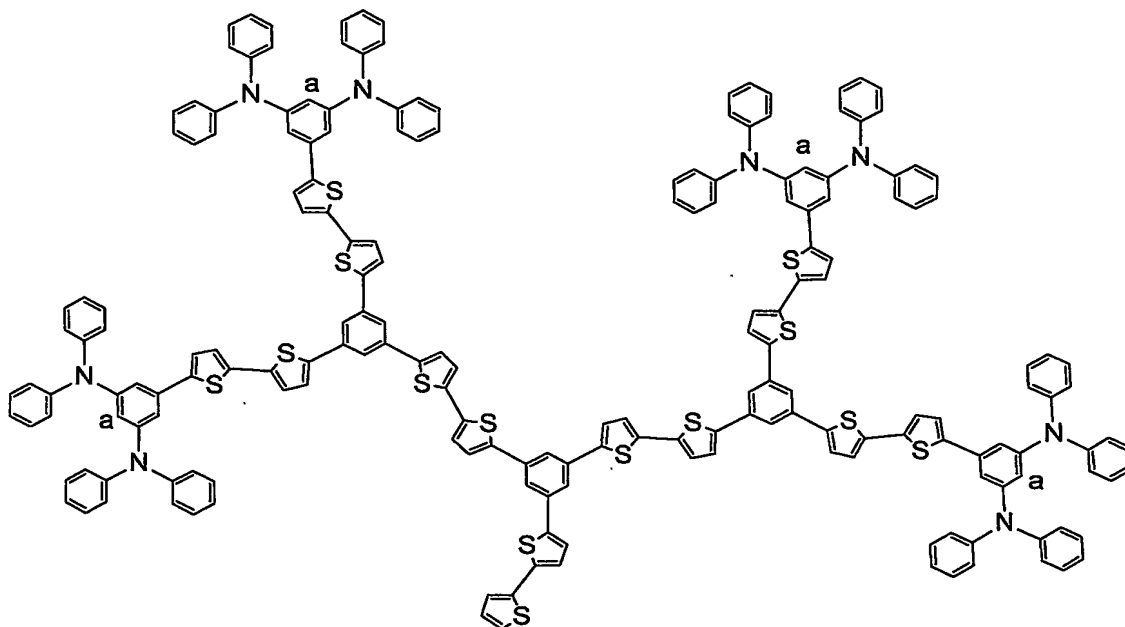
wherein, "a" represents the position of proton Ha, on which

an integrated value obtained by ^{1}H-NMR spectroscopy was

10   evaluated.

<Synthesis of boronic acid derivative of 1st-generation

dendritic polymer represented by the following formula (12)

through conversion, to active group B(OH)$_2$, of α-hydrogen of

the corresponding thiophene ring of 1st-generation dendritic

15   polymer>

(12)
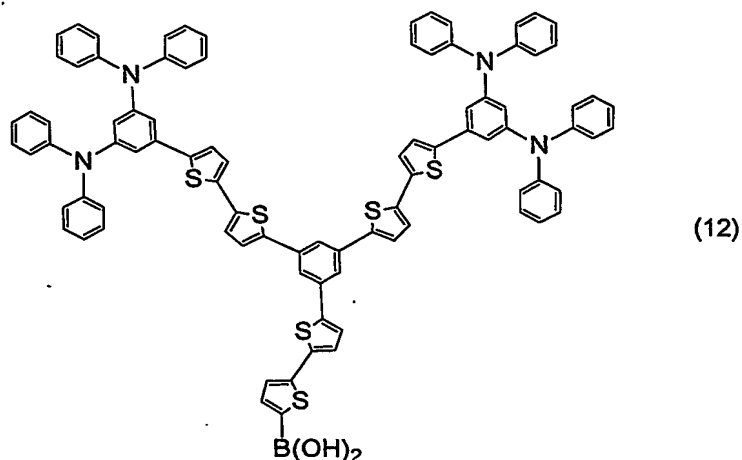
In a nitrogen atmosphere, the 1st-generation dendritic
polymer (1.4 g) which had been produced in Synthesis Example
1-4 was dissolved in dehydrated tetrahydrofuran, and the
solution was cooled in a dry ice – methanol bath. After

5   cooling, a 10-wt.% lithium diisopropylamide/n-hexane
suspension (2.1 g, product of Aldrich) was added dropwise
thereto, and the mixture was allowed to react for one hour.
Subsequently, trimethoxyborane (0.42 g) was added dropwise
thereto, and the resultant mixture was allowed to react for

10   one hour. After completion of reaction, water was added
thereto for hydrolysis. Thereafter, the cooling bath was
removed, whereby the temperature of the reaction mixture was
elevated to room temperature. An aqueous saturated ammonium
chloride solution and diethyl ether were added to the

15   reaction mixture, and the resultant mixture was stirred and
left to stand. The formed organic layer was isolated from
the mixture, and the aqueous layer was subjected to
extraction with a solvent mixture of tetrahydrofuran and
diethyl ether (volume ratio: 1/2). The organic layer

obtained through extraction was combined with the above

organic layer, and the resultant mixture was washed with an

aqueous saturated sodium chloride solution. The mixture was

dried over sodium sulfate, and the solvent was distilled off

5   under reduced pressure, to thereby yield a crude product.

The crude product was recrystallized from tetrahydrofuran/n-

hexane, to thereby yield 0.9 g of the target product; i.e., a

1st-generation boronic acid derivative (hereinafter

abbreviated as "G1-B(OH)$_2$") (pale yellow solid, yield: 63%).

10 The structure of the product was confirmed through ^{1}H-NMR

spectroscopy (solvent for measurement: DMSO-d^6) from the fact

that a peak attributed to the OH proton of the boronic acid

is observed at about 8.3 ppm and that the ratio of the

integrated value of the benzene-ring-originating protons to

15 that of the thiophene-ring-originating protons coincides with

that of the target structure product.

<Suzuki cross-coupling reaction>

In a nitrogen atmosphere, THF (3 mL) and water (0.6 mL)

were added to a mixture of G1-B(OH)$_2$ (0.9 g); 5-(3,5-

20 dibromophenyl)-2,2'-bithiophene (0.12 g) which had been

produced in Synthesis Example 1-1; palladium acetate (4 mg);

triphenylphosphine (14 mg); and sodium carbonate (66 mg), and

the resultant mixture was allowed to react for eight hours

under reflux conditions. After completion of reaction, the

25 reaction mixture was cooled to room temperature, and water (3

mL) was added thereto. The resultant mixture was subjected

to extraction with methylene chloride, and the formed organic

layer was washed with water. The organic layer was dried

over sodium sulfate, and the solvent was distilled off under

reduced pressure, to thereby yield a crude product. The

crude product was isolated and purified through column

5   chromatography (packing material: Silicagel 60 (product of

Merck), eluent: methylene chloride /n-hexane), to thereby

yield 0.47 g of the target product; i.e., a 2nd-generation

dendritic polymer (pale yellow solid, yield: 52%). The

structure of the obtained product was confirmed through [1]H-

10   NMR spectroscopy (solvent for measurement: $CDCl_3$) with

reference to an integrated value at about 6.7 ppm (4H)

attributed to benzene ring proton Ha having two adjacent

nitrogen atoms, from the fact that the ratio of the

integrated value of the benzene-ring-originating protons to

15   that of the thiophene-ring-originating protons, observed at

about 6.9 to about 7.4 ppm and about 7.6 to about 7.8 ppm,

coincides with that of the target structure product. The

weight average molecular weight (Mw), number average

molecular weight (Mn), and molecular weight distribution

20   (Mw/Mn), as measured through GPC were found to be 3,514,

3,385, and 1.038, respectively. These values indicate that

the target polymer has high purity and assumes a single

dispersion state.

<Synthesis Example 1-6> Synthesis of 3rd-generation

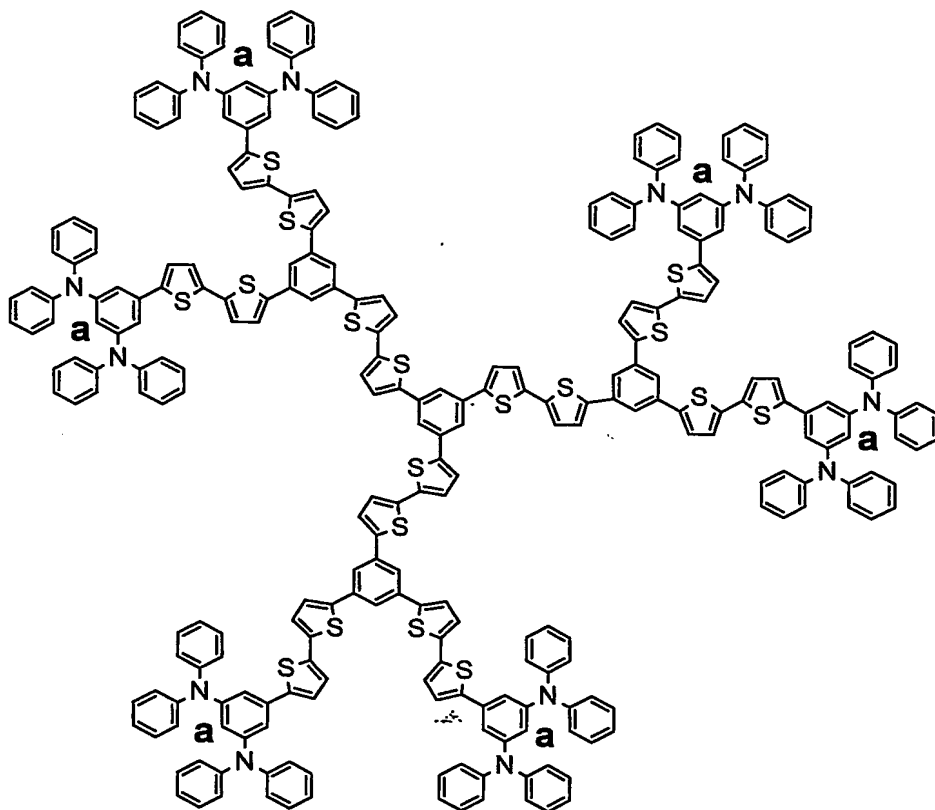25   dendritic polymer represented by the following formula (13)

(13)
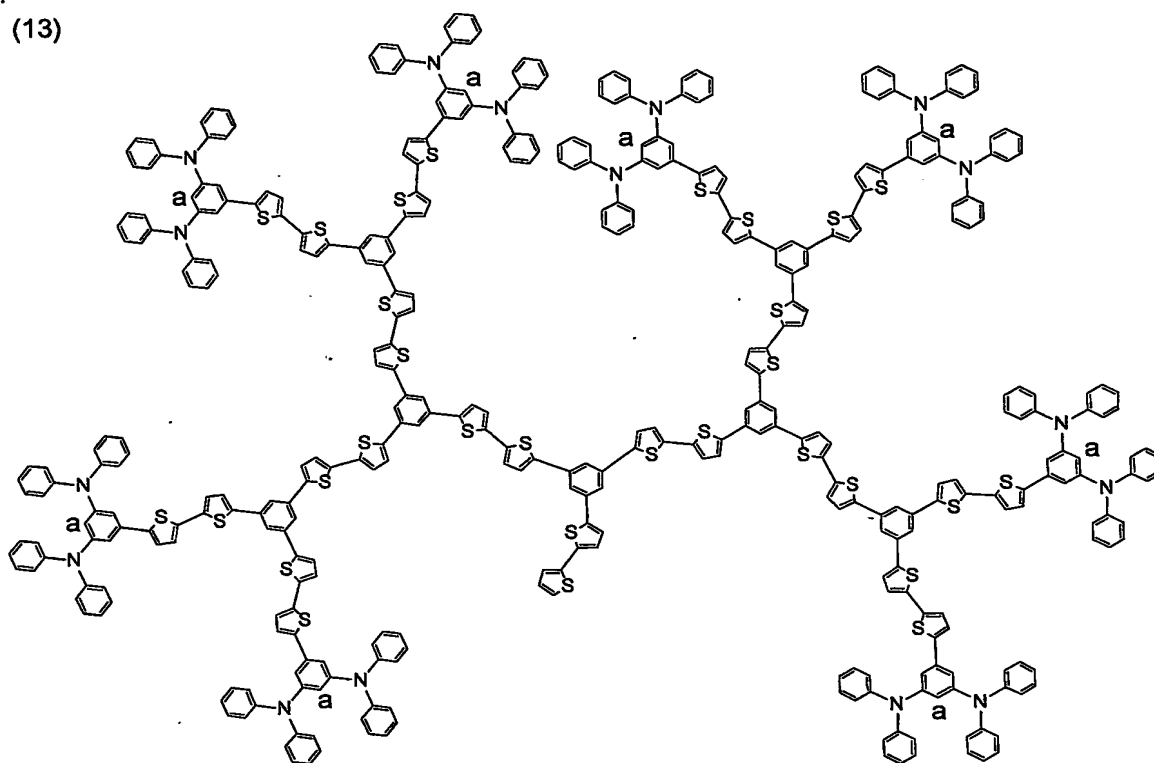
wherein, "a" represents the position of proton Ha, on which
an integrated value obtained by ^{1}H-NMR spectroscopy was
evaluated.

A boronic acid derivative of the 2nd-generation
5   dendritic polymer was synthesized through conversion, to
active group B(OH)$_2$, of α-hydrogen of the corresponding
thiophene ring of the 2nd-generation dendritic polymer which
had been synthesized in Synthesis Example 1-5. Subsequently,
the derivative underwent Suzuki cross-coupling reaction with
10   5-(3,5-dibromophenyl)-2,2'-bithiophene which had been
synthesized in Synthesis Example 1-1, to thereby yield a 3rd-
generation dendritic polymer. In the above synthesis, the
procedure of Synthesis Example 1-5 was repeated, except that
the 2nd-generation dendritic polymer was employed instead of

the 1st-generation dendritic polymer. The structure of the
obtained product was confirmed through ^{1}H-NMR spectroscopy
(solvent for measurement: CDCl$_3$) with reference to an
integrated value at about 6.7 ppm (8H) attributed to benzene

5   ring proton Ha having two adjacent nitrogen atoms, from the
fact that the ratio of the integrated value of the benzene-
ring-originating protons to that of the thiophene-ring-
originating protons, observed at about 6.9 to about 7.4 ppm
and about 7.6 to about 7.8 ppm, coincides with that of the

10 target structure product. The weight average molecular
weight (Mw), number average molecular weight (Mn), and
molecular weight distribution (Mw/Mn), as measured through
GPC were found to be 7,890, 7,610, and 1.037, respectively.
These values indicate that the target polymer has high purity

15 and assumes a single dispersion state.
<Synthesis Example 2> 1st-Generation, 3-branched dendritic
polymer represented by the following formula (bonding of 1st-
generation dendritic polymer to benzene core)

wherein, "a" represents the position of proton Ha, on which an integrated value obtained by ^{1}H-NMR spectroscopy was evaluated.

In a nitrogen atmosphere, THF (6 mL) and water (1 mL)

5   were added to a mixture of the boronic acid derivative of the 1st-generation dendritic polymer (i.e., G1-B(OH)$_2$) represented by formula (12) which had been produced through "conversion, to active group B(OH)$_2$ of α-hydrogen of the corresponding thiophene ring of 1st-generation dendritic

10   polymer" of Synthesis Example 1-5 (1.03 g); 1,3,5-tribromobenzene (68 mg); palladium acetate (15 mg); triphenylphosphine (51 mg); and sodium carbonate (95 mg), and the resultant mixture was allowed to react for eight hours

under reflux conditions. After completion of reaction, the
temperature of the reaction mixture was lowered to room
temperature, and water (3 mL) was added thereto. The
resultant mixture was subjected to extraction with

5   chloroform, and the formed organic layer was washed with
water. The organic layer was dried over sodium sulfate, and
the solvent was distilled off under reduced pressure, to
thereby yield a crude product. The crude product was
isolated and purified through column chromatography (packing

10   material: Silicagel 60 (product of Merck), eluent: methylene
chloride /n-hexane) and subsequently recrystallized from
chloroform, to thereby yield 0.35 g of the target product;
i.e., a 1st-generation, 3-branched dendritic polymer (pale
yellow solid, yield: 39%). The structure of the obtained

15   product was confirmed through ^{1}H-NMR spectroscopy (solvent
for measurement: CDCl$_3$) with reference to an integrated value
at about 6.7 ppm (6H) attributed to benzene ring proton Ha
having two adjacent nitrogen atoms, from the fact that the
ratio of the integrated value of the benzene-ring-originating

20   protons to that of the thiophene-ring-originating protons,
observed at about 6.9 to about 7.2 ppm and about 7.4 to about
7.5 ppm, coincides with that of the target structure product.
The measurement data are shown below. The weight average
molecular weight (Mw), number average molecular weight (Mn),

25   and molecular weight distribution (Mw/Mn), as measured
through GPC were found to be 5,017, 4,667, and 1.073,
respectively. These values indicate that the target polymer

has high purity and assumes a single dispersion state.

^{1}H NMR (CDCl$_3$) 7.48 (s, benzene ring, 3H), 7.46 (s, benzene ring, 6H), 7.43 (s, benzene ring, 3H), 7.22-7.18 (m, benzene ring and thiophene ring, 57H), 7.10-7.08 (m, benzene ring and thiophene ring, 60H), 6.99-6.94 (m, benzene ring and thiophene ring, 33H), 6.90 (d, J=0.8 Hz, benzene ring, 12H), 6.87 (d, J=3.2 Hz, thiophene ring, 6H), 6.73 (t, J=2.0 Hz, benzene ring, 6H).

<Example 1> Organic switching transistor element

An organic thin film switching transistor of a reverse stagger structure containing the dendritic polymer of the present invention was fabricated. FIG. 1 schematically shows a cross-section of the transistor.

As shown in FIG. 1, the organic thin film switching transistor of a reverse stagger structure containing the dendritic polymer of the present invention includes an electrically insulating substrate 1 typically formed of glass; a gate electrode 2 provided on the substrate; a gate insulating layer 3 formed on the gate electrode 2; a drain electrode 4 and a source electrode 5 formed on the gate insulating layer; and an organic semiconductor layer 6 covering these members. The gate electrode 2 is formed of Ta, and the drain electrode 4 and source electrode 5 are formed of Au. The organic semiconductor layer 6 is formed from a 3rd-generation dendritic polymer synthesized in Synthesis Example 1-6 and having hole- and electron-conductivity (represented by formula (13)).

The organic thin film switching transistor was fabricated in the following manner. Firstly, Ta was vapor-deposited via a mask on the electrically insulating substrate 1, to thereby form the gate electrode 2. The surface of the gate electrode 2 was oxidized, to thereby form the gate insulating layer 3. Subsequently, Au was vapor-deposited via a mask on the gate insulating layer, to thereby form the drain electrode 4 and source electrode 5. The dendritic polymer which had been synthesized in Synthesis Example 1-6 (formula (13)) was applied thereto through ink-jet coating, to thereby form the organic semiconductor layer 6. The channel length was 12 μm.

The carrier mobility of the organic thin film switching transistor, as measured through the time-of-flight method, was found to be 3 $cm^2V^{-1}s^{-1}$. The on/off current ratio, obtained through evaluation of current-voltage characteristics, was found to be a level of about 10^6. The obtained carrier mobility and the on/off current ratio were also equivalent to those of a currently employed, similar transistor containing a-Si.

The results, together with those in relation to a transistor of Comparative Example 1 shown below, indicate that performance of an organic thin film switching transistor can be drastically enhanced through employment of the dendritic polymer of the present invention.

<Comparative Example 1>

The procedure of Example 1 was repeated, except that

oligothiophene was used to form the organic semiconductor layer, to thereby fabricate an organic thin film switching transistor employing an organic semiconductor layer formed of oligothiophene.

5   The carrier mobility of the organic thin film switching transistor was found to be 8.5×10^{-3} $cm^2V^{-1}s^{-1}$, and the on/off current ratio was found to be a level of about 10^3.

<Example 2> Light-emitting element

A light-emitting element containing the dendritic

10   polymer of the present invention was fabricated. FIG. 2 schematically shows the element.

As shown in FIG. 2, the light-emitting element containing the dendritic polymer of the present invention includes a transparent glass substrate 11 for fabricating an

15   organic light-emitting element; an electrode 12 formed thereon; a hole-injecting layer 13 and a dendritic polymer layer (hole-transporting, electron-transporting, light-emitting) 14; and an electrode 15, the layers 13 and 14 being provided between the electrodes 12 and 15.

20   The light-emitting element was fabricated in the following manner. Firstly, ITO (indium tin oxide) was formed on the glass substrate 11 for fabricating an light-emitting element, to thereby form the electrode 12 serving as a positive electrode. The hole-injecting layer 13 was provided

25   in the film form from a mixture of poly(ethylenedioxythiophene) and sodium poly(styrenesulfonate) through the spin-coating method at

room temperature. The thickness of the film was 50 nm. The

dendritic polymer layer (hole-transporting, electron-

transporting, light-emitting) 14 was provided in the film

form from a solution of the dendritic polymer which had been

5   synthesized in Synthesis Example 1-6 (formula (13)) in

tetrahydrofuran through the spin-coating method at room

temperature. The thickness of the film was 50 nm.

Subsequently, aluminum/lithium (9 : 1) alloy was vapor-

deposited, to thereby form the electrode 15 serving as a

10   negative electrode. Thus, a light-emitting element was

fabricated.

The light-emitting element was activated through

application of a predetermined voltage, and initial luminance

of emitted light was determined to be 1,500 cd/m^2. The time

15   required for decreasing the initial luminance to the half

value was determined to be 3,000 hours or longer.

The results, together with those in relation to an

element of Comparative Example 2 shown below, indicate that

element characteristics can be drastically enhanced through

20   employment of the dendritic polymer of the present invention.

<Comparative Example 2>

The procedure of Example 2 was repeated, except that

poly(hexylthiophene) was used to form the light-emitting

layer, to thereby fabricate a light-emitting element of the

25   same structure.

The light-emitting element was activated through

application of a predetermined voltage, and initial luminance

of emitted light was determined to be 800 cd/m^2. The time required for decreasing the initial luminance to the half value was determined to be 800 hours.

<Example 3> Organic solar cell element

5   An organic solar cell element containing the dendritic polymer of the present invention was fabricated. FIG. 3 schematically shows the element.

As shown in FIG. 3, the organic solar cell element containing the dendritic polymer of the present invention

10   includes a transparent glass substrate 21; an electrode 22 formed on the substrate; an electrode 24; and a dendritic polymer layer 23 provided between the electrodes 22 and 24.

The organic solar cell element was fabricated in the following manner. Firstly, ITO was formed on the glass

15   substrate 21, to thereby form the electrode 22. The dendritic polymer layer (hole-transporting, electron-transporting, light-emitting) 23 was provided in the film form from a liquid mixture containing copper phthalocyanine and a solution of the dendritic polymer (hole- and electron-

20   conductive) which had been synthesized in Synthesis Example 1-6 (formula (13)) in tetrahydrofuran through the spin-coating method at room temperature. The thickness of the film was 50 nm. Subsequently, silver was vapor-deposited, to thereby form the electrode 24. Thus, an organic solar cell

25   element shown in FIG. 3 was fabricated.

The organic solar cell element was irradiated with the light which was provided from a tungsten lamp and of which

light beams of 400 nm or lower were cut out. Initial energy

conversion efficiency was determined to be 2.3 to 3.0%, which

are satisfactory.

The results, together with those in relation to an

5   element of Comparative Example 3 shown below, indicate that

element characteristics can be drastically enhanced through

employment of the dendritic polymer of the present invention.

<Comparative Example 3>

An organic solar cell element of a structure which is

10   schematically shown in FIG. 4 was fabricated.

As shown in FIG. 4, the organic solar cell element of

Comparative Example 3 includes a transparent glass substrate

101; an electrode 102 formed on the substrate; a charge-

generating layer 103 formed of copper phthalocyanine; an

15   electron-conductive layer 104 formed of a hexazatriphenylene

derivative; a hole-transporting layer 105 formed of a mixture

of poly(ethylenedioxythiophene) and sodium

poly(styrenesulfonate); and an electrode 106, these elements

being stacked in this order.

20   The organic solar cell element was irradiated by light

which was provided from a tungsten lamp and of which light

beams of 400 nm or lower were cut out. Initial energy

conversion efficiency was determined to be 1.7 to 2.0%.

<Example 4> Organic rectifying element

25   An organic rectifying element containing the dendritic

polymer of the present invention was fabricated. FIG. 5

schematically shows the element.

68

As shown in FIG. 5, the organic rectifying element containing the dendritic polymer of the present invention includes a transparent glass substrate 31; an electrode 32 formed thereon; a dendritic polymer layer 33; and an

5   electrode 34, the layer 33 being provided between the electrodes 32 and 34.

The organic rectifying element was fabricated in the following manner. Firstly, ITO was formed through vapor deposition on the glass substrate 31, to thereby form the

10   electrode 32. The dendritic polymer layer 33 was provided in the film form, through the spin-coating method at room temperature, from a solution of the dendritic polymer having hole- and electron-conductivity and produced in Synthesis Example 2 (formula 14) in NMP (N-methylpyrrolidone). The

15   thickness of the film was 50 nm. Subsequently, Li-Al alloy was vapor-deposited, to thereby form the electrode 34. Thus, an organic rectifying element shown in FIG. 5 was fabricated.

The current-voltage characteristic of the organic rectifying element was investigated in the dark. The results

20   are shown in FIG. 6. As is clear from FIG. 6, the element exhibits an insulative property in a range from about −1.3 V to about 0.3 V and a conductive property when the applied voltage is further elevated, whereby excellent rectifying characteristics can be attained.

25   <Comparative Example 4>

The procedure of Example 4 was repeated, except that poly(3-hexylthiophene) doped with antimony fluoride was used

69

instead of the dendritic polymer layer 33 of Example 4, to

thereby fabricate an organic rectifying element of

Comparative Example 4.

The current-voltage characteristic of the organic

5   rectifying element was investigated in the dark. The results

are shown in FIG. 7. As is clear from FIG. 7, the element

exhibits solo conductivity, failing to attain rectifying

characteristics.

***

10   As described hereinabove, according to the present

invention, a novel dendritic polymer serving as an organic

semiconductor material which is isotropic and which exhibits

remarkably high carrier conductivity can be provided. In

addition, electronic device elements requiring carrier

15   conductivity and having remarkably high carrier conductivity

can be produced through a simple production process.